HAL
open science

Specific features of flax fibres used to manufacture composite materials

Christophe Baley, Moussa Gomina, Joël Bréard, Alain Bourmaud, Sylvain Drapier, Manuela Ferreira, Antoine Le Duigou, Pierre Jacques Liotier, Pierre Ouagne, Damien Soulat, et al.

To cite this version:

Christophe Baley, Moussa Gomina, Joël Bréard, Alain Bourmaud, Sylvain Drapier, et al.. Specific features of flax fibres used to manufacture composite materials. International Journal of Material Forming, 2018, 12, pp.1023-1052. 10.1007/s12289-018-1455-y . emse-02015952

HAL Id: emse-02015952

https://hal-emse.ccsd.cnrs.fr/emse-02015952v1

Submitted on 5 Feb 2024

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

International Journal of Material Forming
November 2011, Volume 12, Issue 6, Pages 1023-1052
https://doi.org/10.1007/s12289-018-1455-y
https://archimer.ifremer.fr/doc/00473/58429/

Archimer
https://archimer.ifremer.fr

Specific features of flax fibres used to manufacture composite materials

Baley Christophe [1], Gomina Moussa [2], Breard Joel [3], Bourmaud Alain [1], Drapier Sylvain [4], Ferreira Manuela [5], Le Duigou Antoine [1], Liotier Pierre Jacques [4], Ouagne Pierre [6], Soulat Damien [5], Davies Peter [7, *]

[1] IRDL, UMR CNRS 6027Université de Bretagne-SudLorient Cedex, France
[2] CRISMAT, UMR CNRS 6508Caen Cedex 4, France
[3] LOMCUMR CNRS 6294, Université du HavreLe Havre, France
[4] École des Mines de Saint-Étienne, UMR CNRS 5307, LGFUniversity of LyonSaint-Étienne cedex 2, France
[5] ENSAIT, GEMTEXUniversity of LilleRoubaix, France
[6] Laboratoire Génie de Production (LGP), INP-ENITUniversité de ToulouseTarbes, France
[7] IFREMER, Centre de BretagneLCSMPlouzané, France

* Corresponding author : Peter Davies, email address : peter.davies@ifremer.fr

Abstract :

The use of composite materials reinforced by flax fibres has been increasing steadily over the last 20 years. These fibres show attractive mechanical properties but also some particularities (naturally limited length, presence of a lumen, fibres grouped in bundles in the plant, complex surface properties and composition). An analysis of the available literature indicates that the quality of the composite materials studied is not always optimal (high porosity, incomplete impregnation, heterogeneous microstructure, variable fibre orientation). This paper reviews published data on the specific nature of flax fibres with respect to manufacturing of biocomposites (defined here as polymers reinforced by natural fibres). All the important steps in the process which influence final properties are analyzed, including the plant development, retting, fibre extraction, fibre treatment, preform preparation, available manufacturing processes, the impregnation step, fibre cell wall changes during processing and fibre/matrix adhesion.

Keywords : Composite materials, biocomposite, flax fibre, polymer, processing

Please note that this is an author-produced PDF of an article accepted for publication following peer review. The definitive publisher-authenticated version is available on the publisher Web site.

1/ Introduction

Composite materials

Before discussing the particular case of composite materials reinforced by plant fibres (biocomposites or bio-sourced composites), a brief reminder of the main characteristics of composite materials will be given. The studies cited here refer to ceramic composites, as the first work in this area was focused on ceramic matrix materials before being extended to organic matrix composites. It is important to establish this framework, as the biocomposites tested in many published studies contain significant levels of defects; these develop during manufacturing due to the specific nature of the reinforcement.

At the start of the 20th century the main material question for structural elements was whether to make them in wood or in metal, with the stress level and the environment (maximum temperature, humidity…) guiding the choice. Wood could be sculpted, metals could be cast or machined, and these forming processes are still in use today.

A century later, there is a multitude of materials options for structural components, and the algorithm for material selection can be outlined as follows:

1. The design requirements for the application (mechanical stress level, service temperature, environment, allowable weight…) indicate the base material to use (wood, ceramic, metal alloy or polymer).
2. If a polymer satisfies the requirements, it can be used in the bulk or monolithic state.
3. However, if the bulk polymer does not possess all the properties required (low yield stress, brittle behaviour etc.) it may be reinforced by adding a limited amount of a stiffer or higher strength material, e.g. addition of glass fibres to polymers to improve their stiffness and strength.

This has led to the development of the field of composite materials. The base polymer to be reinforced is the matrix (the continuous phase), the added material is the reinforcement. It should be noted that the composite material (matrix + reinforcement) is not a mixture but a new material with particular properties. According to Naslain [1], a *composite is a multi-phase solid in which two or several constituents are associated in order to provide, at the macroscopic scale and at least in some directions, an original set of properties that the constituents taken separately cannot achieve*.

In this case it is necessary to define:

a- The nature of the reinforcement (ceramic, metallic, polymer or natural material) considering the stress levels in service and the compatibility of the two constituents in terms of their chemical, mechanical and physical properties.

b- The reinforcement content or volume fraction, which governs the composite behaviour.

c- The morphology of the reinforcement. For example the dispersion of fine particles can provide reinforcement while maintaining a homogeneous meso-structure [2][3][4]. Crack deviation and microcracking of the matrix may occur due to the presence of particles [5][6], or phase transformation [7][8]. The presence of fibres, solid materials with a high surface/volume ratio, can provide tensile strength much higher than that of the same volume of material in the bulk form, as discussed by Weibull in a statistical approach to brittle fracture [9]. For fibrous reinforcements the morphology can be described by an aspect ratio (ratio length/diameter). This parameter can be used to distinguish between short (l/d < 1000) and long (l/d > 1000) fibres. If a fibre with a break strength σ_f^r is loaded in tension while held in a matrix over a distance l , with an interfacial shear strength τ, it will break without debonding if the held length is greater than a critical length $l_c = r\sigma_f^r/2\tau$ [10]. If the imprisoned length is shorter than l_c the fibre will be pulled out of the matrix. The fibre ends are favoured sites for damage initiation due to the high strain gradient resulting from differences in elastic properties between fibres and matrix. In a structural component, it is therefore important to reduce the fibre end density. The use of continuous fibres is beneficial in promoting homogeneous stress and strain fields. In addition to the damage mechanisms noted above for particle reinforcement, the use of short fibres can result in crack pinning [11], fibre/matrix friction, and fibre breaks. Many authors have examined the effect of short fibre aspect ratio on fracture toughness [6][8][12][13][14][15][16]. The favoured mechanism will depend on the particular fire/matrix system condidered, and in particular the quality of the fibre-matrix interface. Another important parameter is the material meso-structure. Depending on the

manufacturing process the fibres may be randomly distributed, in layers or perpendicular to the loading direction. This results in varying degrees of orthotropy; skin-core effects are frequently obtained by processes such as injection moulding. When long fibres are used the meso-structure is quite different, as a range of fibre architectures can be produced (unidirectional, cross-ply, biaxial or triaxial weaves, stitched, 3-D assemblies, 3-D weaves…). As a result the damage mechanisms are more complex than for short fibre composites. Failure of fibres involves debonding and friction, which increase failure energy.

d- The interface region between fibres and matrix, also known as the interphase, is the third constituent in a composite material. Despite its small thickness, this region plays a major role in defining all the properties of the composite (mechanical, chemical, environmental…). For this reason, beyond the choice of matrix and fibre for a given application the manufacturing process, which will determine the quality of the interface, is of major importance. The interface must allow the reinforcement to adapt to the matrix. It can be characterized by the fibre/matrix adhesion, based on the interactions (physical, chemical, electrical…) between the two constituents. In practice, the adhesion between fibres and matrix can be evaluated by fracture energy or interfacial shear stress values. Many experimental test procedures have been proposed, the most common are micro-droplet and fragmentation tests (derived from the approach proposed by Aveston-Cooper-Kelly [17].

The main traditional market for flax fibres is the textile industry, but new applications such as the reinforcement of polymers are now growing. For this reason, several research projects focus on the properties of flax fibres.

This paper will only consider composite materials reinforced by flax fibres. An overview of the range of plant fibres available for polymer reinforcement can be found in [18].

The use of flax fibres to reinforce polymers can be explained in terms of their many advantages, such as:

- Their availability in Europe.
- The presence of an industrial sector: active selection of varieties, many experienced farmers, and companies specialized in the extraction of plant fibres.
- The presence of experienced manufacturers of machines dedicated to the cultivation of flax (precision planting, harvesting, tilling, grain separation, baling, combing, carding…).
- The morphology: The flax unit cell can be considered, among plant fibres, to be a long fibre [19]. Its length varies from 13 to 65 mm [20] [21]. The fibres are assembled in bundles in the plant, the bundle length varies from 30 to 90 cm [20].
- The mean fibre diameter (d_f = 16.8±2.7 μm) is similar to that of E glass fibres used for polymer reinforcement. Fibre diameter varies from 12 to 30 μm [20].
- Good mechanical properties [22] and low density (around 1.5), two points which will be discussed in more detail below.

Fibres taken from plants generally show non-linear, inelastic mechanical behaviour [23][24]. A fibre is considered to be a stack of folds formed of complex polymers reinforced by cellulose microfibrils arranged in a helix with an angle of 10° around the longitudinal axis [25]. In a longitudinal tensile test the fibre response will depend on the constituents, but it is also influenced by two mechanisms [23] [26] [27]: a partial reorientation of the fibrils towards the loading direction, and relative sliding of the fibrils. The tensile response is therefore non linear and above a certain threshold the reorientation leads to an increase in stiffness with increasing strain [23][24]. The change in tensile tangent modulus of single fibres has been discussed in [24]. Other studies have described single fibre cyclic loading [26], and showed that the non-linearity reduces with cycling and the fibre stiffness increases. The viscoelastic response of single fibres has also been studied [28].

A recent paper provided a comparison between tensile properties of different batches of flax fibres (characterized under the same conditions with the same test protocol) [22]. The plants (Linum usitatissimum L.), grown in France between 1993 and 2011, represent 50 different batches of fibres (37 of textile flax and 13 from oil seed flax) of 12 different varieties (7 for the textile flax and 5 for the oil seed). The average tensile properties were a Young's modulus (E_{fL}) of 52.5 ± 8.6 GPa (maximum : 75 GPa and minimum : 36 GPa), a failure stress of 945 ± 200 MPa (maximum : 1454 and minimum : 588 MPa) and a failure strain of 2.07 ± 0.45 % (maximum : 3.5% and minimum :

1,6%). These properties are reproducible from one year to the next for the same variety and same location [29] in spite of climate variations.

These fibres are anisotropic, their other properties are: a transverse modulus (E_{fT}) estimated to be 8 GPa [30], a shear modulus (G_{fLT}) estimated to be 2.5 GPa [31] and a Poisson's coefficient of 0.498 [32].

Low fibre density is a key property in reinforcement applications. This value is also important as it is used to estimate fibre fraction and mechanical properties. However, measuring the density of a multi-layer organic fibre with a central lumen is not a trivial exercise, and, in contrast to traditional reinforcements such as glass and carbon fibres, the value obtained is strongly dependent on the measurement technique and conditions [33] [34].

The mechanical properties of a composite ply depend on many parameters such as: the constituent properties (fibre and matrix), their proportions, the degree of crosslinking for a thermoset matrix, or the degree of crystallization for a thermoplastic, the quality of the fibre/matrix interface, the fibre orientation, and the presence of voids, waviness, inclusions or defects.

The characteristic scales for the observation of a ply are usually macroscopic (the ply thickness is 0.1 to 1 mm) or microscopic (between the diameter of a fibre and the thickness of an interphase, i.e. from nanometric to a few microns). However, the meso-structure (scale from a few microns to 0.1mm) [35] should also be examined, it corresponds to the internal organization of the ply (distribution of the fibres in the ply (packing effects), local fibre orientation (waviness), fibre ends (discontinuities in the reinforcement), geometry and distribution of porosities, residual stresses…). This meso-structure has a strong influence on the properties at failure and their time dependence. For example for a unidirectional flax/epoxy ply Coroller et al. [36] have shown the influence of the division of fibres bundles on the longitudinal tensile strength. A more uniform fibre distribution results in a higher failure stress. In addition, the manufacturing conditions will affect the results and a round robin on unidirectional specimens with the same fibre batch but produced in different laboratories allowed the scatter in mechanical properties to be quantified [37]. The latter underlines the need to take into account the close relationship between manufacturing conditions and the meso-structure.

There are many published papers describing mechanical properties of biocomposites reinforced by flax fibres. The matrix polymer may be a thermoplastic such as PLA [38][39], PA11 [40] or PP [41][42]. Many thermoset matrix polymers have also been investigated, particularly epoxies [36][43][44][45][46][44][47][48][49][50][51]. An analysis of these papers highlights the role of the ply meso-structure, in particular the presence of fibre bundles (Figure 1) [36][52], the non-uniform fibre distribution and the twist (Figure 2), [43,44][47][49][51], and impregnation difficulties resulting in high void content e.g.7.1 to 19% [51] and 4 to 33% [50], despite high compaction pressures (Figure 3). Some authors have reported a significant reduction in porosity following chemical treatments of fibrous preforms [48].

Figure 1. Microscope image of section perpendicular to fibres in unidirectional composite, showing individual flax fibres and bundles [53]

Figure 2. Quasi-unidirectional flax preform made up of twisted fibre assembles.

The use of preforms made up twisted fibres (Figure 2) results in heterogeneous ply meso-structure (spatial distribution of fibres) and voids for some matrix polymers.

Figure 3. Upper: Example of lay-up of unidirectional flax plies impregnated by a thermoplastic matrix (PP-AMPP) manufactured by film stacking, showing interlaminar voids and a poor spatial fibre distribution through the ply thickness. Lower: Example of a lay-up of unidirectional flax impregnated by thermoplastic matrix (PP) manufactured by compression moulding, showing good material quality [41]**.**

This paper presents a literature survey aimed at highlighting the specific nature of flax fibres and their use as polymer reinforcement. It is not intended to be an exhaustive review, but will focus on the following points: specific features of flax fibres in terms of morphology, compatibility with different matrix polymers, preforming techniques (mesh, layer…), manufacturing techniques and the resulting properties.

2/ Particularities of flax fibres

2.1. Plant growth and fibre development. Stem architecture.

The term "plant fiber" refers to plant tissues that play a role in supporting the plant or transporting nutrients. Observation of a section across a flax stem shows a structure which is similar to that of composite materials [54][21]. Flax stems are reinforced by bundles of elementary fibres which are around the outside of the stem. This organization allows the plant to resist flexural and torsion loads applied by wind and rain. These support materials are used in the textile industry and for composite reinforcement. A flax plant produces between 15 000 and 50 000 elementary fibres [20].

In general, the life of a plant can be defined by five stages: Germination, growth, flowering, seed formation, and aging. Plant development takes a well-defined period, (100 days for flax), under meteorological conditions which vary in terms of temperature (flax grows at temperatures above 5°C), rain, sunshine and daylight. This results in fibre property differences along the stem [55].

Flax bast fibres are primary phloem fibres and originate from procambium, close to the apical meristem. Bast fibre initiation is coordinated with other tissue formation, including xylem components and leaf primordia.

Throughout the growth of the plant, the fibres form around the outside of the stem and in four distinct steps:

1/ Fibre-cell multiplication at the top of the stem [56]

2/ Intrusive elongation in the top 3-5 cm of the stem [57][58]

3/ Fibre expansion and thickening of the walls below the snap point, a zone defined in [59]. The snap point is located 6-8 cm from the top of the plant, where the stem changes its mechanical properties. Above this point, the stem is soft, while below it, the stem is stiff.

4/ Structuring of the walls: Thickening proceeds for around 2 months, almost to plant maturity [20][60]. Changes in the secondary cell wall stiffness have been followed during growth by AFM [61].

Following the growth step, the flax plants are uprooted at maturity. The Flax Technical Institute (ITL) has proposed a maturity criterion for flax plants based on the sum of the accumulated temperatures after seeding [62]. The next step is dew retting, which degrades the bonds between the fibres in order to facilitate mechanical extraction.

2.2. Retting

Abandoned in Western Europe since the 1970s, water retting is still used, despite its eco-toxicity, particularly in Asia and Africa, to facilitate the extraction of hemp, jute or kenaf coconut or sisal fibres. This process, if well controlled [63], produces a much higher quality product with more uniform fibres. However, it causes water pollution, with organic acids and other fermentation products releasing a nauseating odour, and requiring treatment before discharge into rivers. For European flax and hemp, dew retting is favoured. The aim of dew retting is to facilitate the extraction of the fibres by the degradation of the cortical tissues of the stem surrounding the fibre bundles. During this natural biological process, flax stems are colonized by fungi and bacteria, some of which will have already settled on the standing plant [64]. These microorganisms secrete enzymes, which accelerate the degradation of the polysaccharides of the plant, which makes it easier to extract the bundles during scutching. Nevertheless in the case of over-retting, parietal cellulosic components can be affected [63] under the action of cellulase enzymes.

The control of the retting time is critical; organoleptic criteria, such as the as homogeneity, colour, resistance to manually applied tensile load, or ease of division of bundles into unitary fibers, are widely used by hemp and flax growers to estimate the retting degree. In addition, the ease of fibre extraction and the cleanliness of the fibres are also observed. Retting is dependent on the stage of development at which the flax is pulled out [65]. Indeed, after flowering, deposition of lignin gradually increases in the fibre bundles, creating cohesive bundles and making the retting more difficult, consequently, pull-out during flowering may be preferred [65]. A suitable control of the retting time is a preponderant parameter because it determines the quality of the final fibres, of scutching productivity, and composite performance, the fibre divisibility being strongly affected by retting degree. An homogeneous retting favours the production of fine technical fibres [66] [65]. Figure 4 shows how flax colour changes with retting time

[67]. Samples were taken after 1 day (R1), 5 days (R2), 9 das (R3), 14 das (R4), 16 days (R5) and 19 days (R6). R6 is the optimal retting time. Note that retting time depends on micro-organism development, and hence on weather conditions, retting was particularly short for these tests (weather conditions are given in [67]. The colour of R1 fibres, which were retted for 1 day, was light green-yellow whereas the colour of R6 fibres, which were retted for 19 days, was dark grey. Colour changes can be explained by biological growth [64].

Figure 4. Photograph of flax fibres samples with different degrees of retting. From unretted sample (R1) on the left to retted sample on the right (R6) [67]

The impact of retting on fibre and cell walls properties is still not completely understood, but some information is available in the literature. Some authors found no fibre mechanical property changes during the flax retting process [68] [69], whereas other teams clearly showed an increase of single fibre performance with increasing retting time [67,70,71]. In the biochemical sense, retting may lead to a modification of the parietal composition due to enzymatic action. A combined decrease of pectic components [65] [72] and increase of cellulose [73] [74] is generally observed. At the same time the crystallinity of cell walls seems to increase for both hemp and flax [75] [76] [77] but interestingly, in the case of over-retting, a decrease in the degree of cristallinity is observed for hemp fibres, due to enzymatic alteration of cellulose during prolonged time in the field [63]. Nevertheless, measurements of crystallinity changes must be taken with caution due to the calculation method, which is generally influenced by the non-cellulosic component content; the degree of crystallinity measured is relative and highly dependent on the amount of amorphous component, which evolves during retting due to the progressive degradation of middle lamellas.

To conclude on this section, the retting step is of importance not only for fibre element morphology, and especially diameter and divisibility of bundles, but also for the structure and performance of plant cell walls. In addition, retting degree has a strong impact on scutching conditions, and may initiate structural defects such as kink bands. Thus, Aslan et al. [78] observed changes in the tensile response of a green (non-retted) flax behaviour [24][79], as opposed to a retted, scutched and then refined flax, explained by the creation of defects due to mechanical treatments (scutching and refining). These results were confirmed by Lefeuvre et al. [29] who have studied the performance of Marylin flax fibres after growing during years with very different climates and therefore with extreme degrees of retting. They have demonstrated significant decreases in mechanical performance for fibres scutched at high speeds, due to under-retting.

2.3. Mechanical treatments: extraction, fibre cleaning

To be used in composite applications (and textile), fibres have to be extracted from the stem. Industrial production of flax fibres from plants is performed by a decortication process, also called scutching. The aim of this step is to extract the fibres from the stem by removing the woody core [80][81].

Scutched fibres appear as aligned long individual fibres (or small bundles) containing a small amount of shives, according to the efficiency of the scutching process and the degree of retting. Shives are formed by the fragmentation of the woody core. During scutching, some parts of the plants are withdrawn from the material flow and fall into a secondary circuit. These fibrous parts are called tows. They are made of misaligned and entangled flax fibres, and contain a large quantity of shives [82]. Scutched fibres have the highest economic value of all flax products. Scutched flax can be directly hackled to be used for yarn spinning. Tows have less value as they must undergo further opening and carding operations to be cleaned of shives and aligned, prior to spinning.

The forming of fibres for composite reinforcement in preforms will be discussed in Section 3.

2.4. Variability and reproductibility of flax fibre properties.

Plant selection today is not based on the mechanical properties of fibres. The main end use is still the textile industry, so new varieties are developed based on the needs of farmers and fibre extraction, with different criteria [83], the main ones being the quantity of fibres produced, resistance to weather conditions and to disease. In France a new variety is protected for 20 years, so there are regular changes in the varieties produced.

Many parameters influence fibre properties [84][29][79][82][83][85]: The plant (species, variety, genetic characteristics, seed quality…), growth conditions (physico-chemical and biological characteristics of the soil, previous crops, water availability, temperature, sunlight, wind, daylight…), farming practices (soil preparation, seeding date, mode and density of seeding, organisation of the field, fertilization, treatments…), pulling date or cutting, plant dehydration, retting, plant storage, extraction and refining of the fibres (scutching, combing, carding…). Some of these can be controlled, others such as those which depend on the weather, cannot (rain, sunshine, wind, temperature, debydration, retting).

2.5. Presentation of the fibre material (the basis of the preforms)

For the textile industry, the main product from scutching plant stems (flax or hemp) is long fibres. The fibrous by-products obtained during extraction of these long fibres are tows. A tow is a bundle of a small number of fibres held together by mechanical contacts, some entanglements and electrostatic forces. Tows were used to light fires from sparks produced by flints and are still used to make wooden boat hulls waterproof. Previously considered to be a waste product, there is renewed interest in this material for its mechanical properties. In fact the fibre lengths can be nearly as long as those of the long fibres once they have been disentangled and aligned [82]. They can thus be used in a similar way to long fibres, even though they are mainly employed today to produce mats for sandwich materials.

In order to produce long fibres for the textile industry the extraction conditions must be satisfactory for the farmer, i.e. produce a sufficient quantity of long fibres and as few tows as possible. The long fibres are then combed (alignment of fibres and removal of the remaining seeds) in order to obtain a silk-like texture. The mechanical properties required for the fibres are simply those needed to resist mechanical loading on textile machines. For composite materials however, the requirements are much more severe, and include mechanical, temperature, and environmental resistance. Barbulée [86] has shown for example that the moisture content in flax stems affects the failure stress of individual fibres. He also showed that the environmental conditions during scutching affect the physical and mechanical properties of fibre bundles.

3/ Production of composite reinforcement from plant fibres

3.1 DIfferent reinforcement architectures

Composite materials used in structural applications, i.e. where loads are high, are usually reinforced by continuous fibres; mainly glass or carbon. The previous section underlined the particular nature of plant fibres, which are not continuous, so they require particular attention during preform manufacture. For other applications, the composite can be reinforced by short fibres, so traditional polymer forming methods (injection, compression…) can be employed. The two types of material are thus quite distinct with respect to the mechanics of manufacture.

It is necessary to study the behaviour, the deformation, and the formability of fibrous reinforcements at certain steps of the forming process when the matrix is not yet in place (LCM processes, Liquid Composite Molding). This requires the study of preforms. In addition, for other processes the matrix is present but in liquid form, so the physical behaviour is also governed by the fibres.

The reinforcement can be studied at three scale levels:

- fibre: microscopic scale;
- roving, or the unit cell which defines the meso-structure: the mesoscopic scale;
- composite component: macroscopic scale.

With respect to the forming process, different types of study can be performed at these different scales, with strong connections between them.

There are various ways to classify textile structures, according to:

- Geometry: 1D, 2D, 3D (linear elements), 3D (planar elements)

- The number of axes defining their orientations: non-axial, mono-axial, bi-axial, tri-axial, multi-axial.
- Manufacturing technology: Weaving, knitting, braiding, non-woven.

All these structures can be produced with plant fibres. In the following paragraphs, the development of the different architectures will be presented, highlighting the particular difficulties caused by this type of fibre.

To manufacture structural composite parts, long aligned and continuous fibre reinforcements are used, as shown by numerous applications based on E-glass or carbon raw material. With these synthetic materials, yarns are constituted of a large number of multifilament, highly aligned with no (or low) twist. From these yarns, fabrics can be manufactured by classical textile technologies. Due to the high added value of the applications in which composite parts can be encountered, low production speeds can be accepted, to limit or prevent the appearance of manufacturing defects and material losses on these twist-less yarns which tend to fibrillate during the preform manufacturing, as illustrated on figure 5. [87][88].

Figure 5. Defects during the weaving process. Left: Broken free glass fibres [91]. Right: broken carbon monofilament [92]

On the contrary, for lower added value textiles (clothing), the use of yarns with lower linear density, strongly twisted [89], if it is not doubly twisted, allows higher manufacturing production rates (higher weaving speeds for example) to be achieved, and fabrics without defects, but with performance that is sufficient for these applications. Particularly, these yarns are not designed to be impregnated by a resin as in the case of composite reinforcements. Manufacturing optimised composite reinforcements for load bearing applications requires the optimisation of several manufacturing steps, which may be challenging as the goal consists of manufacturing preforms as well-aligned as possible from yarns composed of fibres of finite and highly variable length. Yarns also need to be highly permeable to ensure a good penetration of the resin between the fibres or bundles, which is a significant challenge.

With these objectives, we will dissociate in this section the technologies associated with non-woven products from those concerning the alignment of fibres that require the manufacturing of yarns. The deformability of preforms will then be addressed.

Some recent studies have proposed an alternative approach to reinforcement design [90][91][92]. This is based on depositing a unidirectional (UD) layer of flax yarns on a porous paper layer. The paper layer acts as a binder which not only improves manipulation of the loose UD yarns (when transporting them and placing them in the mold) but also maintains their alignment (under pressure or viscous forces arising during LCM (Liquid composite molding)). This type of stacking is not detailed in this article.

3.2 Non-woven (2D)

Although researchers have recently focused on highly aligned plant fibre reinforcement structures [93][94][95][96] for the manufacture of load-bearing composites components, Shah [97] has used an Ashby approach to show that non-woven fabrics can be very attractive in terms of tensile properties per unit cost. Non-woven fabrics or mats are the most common form of reinforcement used in natural-fibre composites [98] due to the costs involved and also to their ability to combine a good acoustic absorption with higher mechanical properties [42] in only one product, compared with loose fibres. Thanks to these properties, non-woven biocomposites are becoming a major asset to the automotive industry for a variety of applications. This is due to their light weight, sound efficiency, flexibility, versatility and easily tailored properties, together with low process and materials costs and an attractive cost/performance ratio.

Process

Das et al. [99][100] have described several technologies to manufacture non-woven fabrics, defined [101] as sheet or web structures bonded together by entangling fibres (and by perforating films) mechanically, thermally or chemically. Short fibres extracted from flax straw have great variations in length and linear density and are the main raw material of non-woven reinforcements. They may have high dust content and are either smooth or stiff. They have relatively little cohesion when formed into a web in contrast to fibres such as wool or cotton for example. Webs are formed either mechanically by carding or aerodynamically. Bonding of webs can be achieved by water jet, needle punching, stitch bonding, adhesive bonding, etc. [102] [103][104]. The needle-punching method is probably

the most suitable method for producing thick non-wovens from flax fibres. The retted, scutched or opened, flax fibres can be used without any chemical treatment. The flax fibres are then carded to form a thin web. The carded web is then made into a thicker batt by the cross-laying or parallel-laying methods. This fibre batt is then consolidated on a needle-punching machine to form the final flax non-woven mat [102][103][104] as shown by figure 6. Hybrid non-woven composites have been prepared by researchers by using blends of synthetic fibres, which provided a good basis for high product quality. By mixing the two composite components before the consolidation, a proportional distribution and a good wetting of the reinforcing fibres can be ensured. Short fibre reinforced and non-woven flax/PP blend composites were prepared by carding and needle punching and analyzed in [42][105][106][107].

Figure 6. Upper: Samples of flax nonwoven fabrics (areal density of 330 g/m^2) [109].

Lower: Cross-section of Flax/PP non-woven fabric after needle-punching [110].

Properties.

Physical properties such as surface mass, density, and thickness play an important role for different potential applications of non-woven materials. Ultimately, these characteristics govern many functional properties of non-wovens such as thermal and noise insulation, water absorbance, resilience, compressibility, filtration, etc. So, we should have knowledge of the processes which are suitable for obtaining a given level of surface mass, density and thickness of non-wovens. The most important characteristic of all non-woven materials is the tensile strength. The tensile properties of needle-punched non-woven fabrics are influenced by the fabric structural parameters, such as the fabric density, the amount, and depth of fibre entanglement resulting from the fabric formation process and fibre properties [104]. The increase of the tensile strength as a function of the areal density of needle-punched flax non-woven was shown by Gnaba et al [109] and Anandjiwala et al. [108]. The tensile properties of non-woven fabrics are different in both directions of the fabric due to structural anisotropy resulting from the process of fabric formation. The practice of producing non-wovens, by web formation and cross-lapping, results in different strengths in the machine direction (MD) and cross directions (CDs), respectively. Fages et al. [109] have studied the tensile properties of flax/PP blend needle-punched heat bonded fabric and they showed that when the proportion of PP fibre increased, the tensile strength increased in the MD and elongation increased. The tensile properties are mainly influenced by needle-punching parameters (depth of needle-punching and needle-punching density). Gnaba et al. [110] have recently demonstrated for Flax/PP non-woven that an increase of the maximum tensile strain can be related to the increase in the needle-punching density. In addition, increasing the needle-punching density leads to a decrease of the anisotropy ratio of the tensile behaviour between the MD and the CD.

3.3 Rovings and yarns for aligned preforms (1D, mono-axial)

Yarn strength is the main property for yarn quality evaluation. Sufficient yarn strength is necessary to manufacture fabrics by weaving or braiding. For natural fibre yarns with too many short fibres with a low (or null) twist level, the tensile failure mechanisms of the yarn are dominated by fibre slippage [111][112]. Many studies have been performed [113][114][115][116][117][118] [119][120][121] to improve the understanding of yarn failure. Parameters at the fibre scale such as the length, distribution of fibres lengths in yarns, and fibre linear density have received particular attention. It is well known that when yarn breaks, fibres may also break or slip in the yarn breaking section. This depends on the critical slipping length of the fibres [121][122][123]. These studies, essentially performed by mechanical modelling [113][114][116][117][118], do not take into account any twist, and assume that all the constituent fibres are completely straight and parallel to the yarn axis. Without a strong cohesion between these staple fibre bundles, slipping occurs and the yarn strength remains low. The variability of tensile properties without a real cohesion between fibres is very high, as shown in [124][125][126]. In this section, three technologies to increase this cohesion are described: twisting by using conventional ring spinning; addition of a binding agent and cohesion by wrapping/comingling/or micro-braiding.

Design and manufacture of flat aligned fibre flat yarns by the mean of an adhesive agent

The long natural technical fibres that are generally considered for reinforcing structural composite parts possess an average length of about 300 mm. Because of their finite length, the technical fibres (flax, hemp), cannot be treated in the same way as synthetic fibres of infinite length such as glass or carbon. However, the biochemical components such as pectins can be used to assemble unidirectional tapes [127].

After the different preparation steps described in the previous section leading to slivers of calibrated linear mass, a spinning step giving cohesion to the technical fibres is performed, because the slivers cannot sustain the different loads applied to them during the textile construction processes such as weaving, breading or knitting. This increases the level of torsion of the fibres and as a consequence the level of tensile resistance of the yarn. However, providing torsion to the fibres within the yarn may lead to difficulties of impregnation of the core of the yarn and to a reduction of the tensile properties at the composite scale [128][129]. Spinning is also a step that consumes a large amount of energy (23 GJ/T) in comparison to scutching and hackling (9.39 and 2.23 GJ/T respectively). As a consequence, the amount of energy required to produce a reinforcement fabric with such yarns (86 GJ/T) is higher than that needed to produce an equivalent product from glass fibres (55 GJ/T) [130].

To maximise the high potential of natural fibres for the reinforcement of composite materials, it is therefore recommended to keep the fibre bundles as aligned as possible and to maximise the fibre volume fraction. In the case of woven fabrics or braids, the use of flat yarns such as the ones that are generally used for synthetic products should be promoted to reach high covering factors and therefore high fibre volume fractions. To achieve this goal, the technical fibres need to be bound together so that they can sustain the loads they are subjected to during the textile construction process. Figure 7 shows a detailed view of flax bonded by an adhesive yarn. Different types of adhesive may be employed. Generally, the manufacturers do not indicate the type of adhesive they use. Several solutions are already used in the textile industry to bind the fibres and avoid any fibrillation. They are based on techniques already used to apply sizing to glass or carbon roving type yarns. This consists of pulling the roving or the sliver through a bath of an adhesive solution and pressing out the excess between compressive rollers. The adhesive solutions can be either synthetic or bio-based. Ideally, the adhesive should be removed at the end of the textile construction process with a minimum impact on the environment. Different commercial alternatives can be encountered. Of course epoxy based solutions (that can be partially bio-based), potentially of the same nature as the epoxy that could be used to manufacture the composite part, can be considered [131]. It is also possible to use products such as the ones currently used by the textile industry to prepare the warp yarns. PVA adhesives are widely used in the textile industry, particularly in North America as a warp sizing agent. PVA based formulas are also available in large quantities on the market [132]. Natural polymers can also be considered as adhesives. As an example, formulated potato starches are used and could be considered to bind natural fibre bundles [133][134]. Other substances called gums have adhesive properties and can also be considered [135]. They are extracted from the bark of trees or shrubs such as the ones of the pea family [136]. One can cite as an example gum tamarind [137] which was used as a binder with sisal fibres [138], or locust bean gum and Arabic gum which are used as sizing agents for textiles [139].

Ideally, it is important to remove the binding agent applied to the yarn for the textile construction process. The removal of the agent depends on its nature. As an example, starch based adhesives can be removed by using catalytic action of enzymes. For water soluble sizes such as PVA or certain gums such as Arabic gum, it is possible to wash the textile with high amounts of hot water. However, the water becomes polluted by the sizing agents and needs to be treated, recycled or used for gas generation [140].

Figure 7. Flax yarn assembled by adhesive bonding

Cohesion by Twisting

Spinning is the process that is the most commonly used to produce continuous twisted yarns of a desired size from fibrous materials. Long and short staple spinning can be distinguished. Short staple spinning machine processes fibres such as natural fibre [141]. An extensive range of spinning techniques were developed during the twentieth century and their classification was described in [142]. At a high twist level, fibre slippage in the yarn is prevented by the high frictional force between the fibres. In this case, the yarn failure is mainly due to fibre breakage. Yarns are characterized by the direction of twist (S or Z-directions), by the twist level (expressed in turns by meter (TPM) or with the twist angle), and by their linear density. The level of fibre alignment as a function of twist level can be estimated by the Krenchel fibre orientation factor [128][143]. Clearly, the fibre alignment in a single yarn reduces when the yarn twist increases, as shown by Gu et al. [143]. Yarns manufactured from short fibres do not have adequate strength for handling unless a sufficient level of twist is applied. The twist required for achieving sufficient yarn strength for processing determines the level of fibre alignment of the single yarns. The influence of twist level on the strength of natural fibre yarns was studied by several authors (Figure 8) (identified at the dry scale) but also on the strength of composites manufactured from these yarns. At the scale of the composite the influence of twist has for effect to decrease the tensile strength as described in [129][43][144]-[145]. However, it is very difficult to

dissociate the influence of twist level during the process of impregnation (for example on the permeability) and the influence on composites characteristics. At the dry scale, on flax yarns of 210 tex, Goutianos and Peijs [129] showed that very low twisted yarns exhibit a very low strength. Ma et al. [146] have studied the effect of different twist levels (20, 60 and 150 turns per meter, tpm) on the tensile strength of un-impregnated sisal yarns (with a linear density of 1250 tex) which first increased and then started to decrease when a critical twist level (90 tpm) was reached.

Figure 8. Fibre spinning (left) [147]**. Right: Typical effect of twist on yarn strength** [128]

The effect of twist on the yarn tensile strength was also described by Shah in [128]. Results from an analytical model were compared with experimental data given by Goutianos and Baets [129][43]. Few experimental data that consider significant variations of twist levels or linear densities are given in the literature. On figure 9, the effect of twist level is shown on the tenacity and the deformation at break identified during tensile tests of 500 and 100 tex flax yarns at the GEMTEX Lab [148]. The influence of the twist level on the tenacity follows the typical effect described in figure 8, but also depends on the linear density. An increase of the twist level results in an increase of the deformation at break, which can be significant.

Figure 9. Influence of twist level on Tenacity (Left) and deformation at break (Right) of flax yarns.

Cohesion by wrapping/comingling/micro-braiding

The wrap spun yarn consists of twist-less staple fibres wrapped by a filament or a fine thread (Figure 9, left). The wrapping filament applies the fibre-to-fibre pressure that is required to create the friction between the fibres and thus the yarn strength [149] [150][151]. Because of the lower fibre-to-fibre pressure generated by the wrapping filament in comparison to the one generated by the twist, wrap spun yarns generally exhibit lower tensile strength and are less compact than the ring spun yarns at their optimal twist level [111]. Zhang et al. applied this technology with flax and hemp staple fibres wrapped by a PP multifilament yarn. This co-wrapping technology was also presented in [93] with Hemp/PLA or by Jiang et al [152] for flax/PP commingled yarns.

Micro-braiding, another technique to assemble staple fibres can also be considered. Jute and sisal micro-braids were manufactured and described in [153][154]. A tubular braiding machine was used to produce micro-braid yarn using a continuous jute yarn inserted axially and a polymer yarn as the matrix material braided around the reinforcing jute thread [153]. This technology, illustrated in figure 6 (right), has also been used for hemp/PLA micro-braided yarn by Kobayashi et al. [155].

To manufacture natural hybrid yarns, the third possibility described in this section deals with commingled yarns by the friction spinning system, DREF-3 (figure 10). Natural fibres can be fed in a rectilinear way, via a tensioning unit, into a spinning device. The straight path of the yarn ensures that no filament damage occurs. Above the friction drums there is a drafting device with an opening unit. After feeding, slivers are opened-up into individual elements by a pinned beater and then transferred to the yarn forming zone to wrap over the core flax yarn.

Figure 10. Left: warping staple natural fibres with a thread [111]**. Right: Micro-braiding technology** [155]**. Below: DREF-3 spinning system** [156][157]

These technologies are used intensively to manufacture hybrid yarns with thermoplastic polymer. In these hybrid yarns, the reinforcing components based on natural fibres form the core of the structure and thermoplastic polymers are wrapped (by wrapping, micro-braiding or DREF-spinning) over the core flax yarn. Bar et al. [156][157] have used this technology with Flax/PP materials. These commingled yarns with thermoplastic polymers improve the

quality of impregnation of the composite material during the thermo-compression step. Alagirusamy et al. [158] summarized various techniques of hybrid yarn manufacturing and explained their effectiveness as thermoplastic composite reinforcing materials. These technologies are also used for synthetic fibres as described in [159][160].

3.4 Fabrics made from plant fibres (2D-3D, mono-axial to multi-axial)

The definition and properties of textile reinforcements are essential factors during composite manufacturing and for the performance of composite materials. The architecture of the reinforcement controls the deformability of the preform during the first step of the RTM process [161]. The porosities (size and distribution) are also key parameters that control the injection process. For the specification of composite materials, load transfer from the matrix to the reinforcement is governed by the fibre orientation, which plays a main role in the composite stiffness. Fibre direction and fibre volume fraction can be managed during the manufacturing process of the reinforcement by textile technologies such as weaving, knitting or braiding. Yarn is converted into fabrics by using these textile technologies. The processes of interlacing, interlooping, braiding, fitting, laminating, and bonding involving usage of yarns is called fabric construction and the resultant material is called the fabric.

The fabrics obtained by these technologies are considered as 2D as the fibres are almost oriented in one plane. At the level of un-impregnated fabrics, weaving yarns into fabrics for easier handling, for example, introduces fibre crimp, which reduces the mechanical properties of the reinforcements. Other textile variabilities such as yarn spacing, yarn path waviness, and wrinkling can also significantly influence subsequent properties [162]. Misnon et al. [163] have shown that for two woven hemp fabrics with the same textile properties (crimp, areal density, linear density of yarns, warp/weft density) the differences in their tensile strengths and tensile moduli are not significant. Some characterization at the level of flax-based woven fabrics are presented in [164][165][166] for the shape forming. Bensadoun et al. [144] have reported on the changes in tensile moduli and tensile strength of composites manufactured from nine flax-fabric architectures (mat, plain weave, twill, quasi-UD, UD. . .) with different areal densities. A multi-level approach (tensile behaviour of un-impregnated yarns and fabrics and composites) was proposed recently by Blanchard et al. [126], and they showed that the wide variability in terms of tensile properties recorded at the scale of flax-fibre yarns decreases at the scale of fabrics and composites. The mechanical and damping properties were measured for unidirectional, 0/90 and twill 2/2 flax fibre composites containing 40 vol% of fibres in an epoxy matrix by Duc et al. in [167]. On 3 different quasi-UD fabrics weaved from flax yarns with similar linear densities but different twist levels, Omrani et al [124] pointed out the influence of the weaving process on the tensile behaviour of flax yarns and fabrics. The degradation during the weaving can be observed on the flax yarns and the twist effect can help to reduce this degradation. From twisted flax yarn (350 Tex, 185 TPM), Xue et al [168] detailed the manufacturing of a non-crimp biaxial weft-knitted fabric. The influence of treatment with sodium hydroxide (NaoH) applied on yarns was studied on the tensile properties of the flax yarns, biaxial weft-knitted reinforcements, and at the scale of flax composites. Woven and braided textile structures are widely used as the composite reinforcements. In a woven structure, the warp and weft directions are interlaced at 90° to each other. Biaxial braiding structure has two principal sets of tows called bias tows. Compared to woven fabric the braid angle is its main characteristic. The braid angle is defined as the angle between axial direction and bias tow and is in the range 5° to 85°. From flax/PA12 commingled yarns the production of biaxial braids with a braiding angle of 35° was presented by Jacquot et al [169] (Figure 11). The formability behaviour was analysed and compared to woven fabrics made with the same yarns.

These studies concern mostly 2D reinforcement, but some new developments of weaving methods for 3D-woven preforms are appearing in the literature. These are mainly manufactured from glass, carbon, polyester or aramid fibres. Lansiaux et al. [148] (figure 12) have recently described the feasibility of realizing 3D warp interlock fabrics from flax flat yarns, and analyzed the influence of architectural parameters of these 3D-reinforcements on the mechanical parameters.

Figure 11. Left: Braiding Loom. Right: Biaxial braids from Flax/PA12 yarns [148]

Figure 12. Manufacture of 3D-warp interlock from flax rovings [148]

3.5 Preform deformability

Shape forming of different textile architectures manufactured from aligned fibre flax yarns was demonstrated [165][169][170] from woven fabrics or braids. Globally, the challenge associated with shape forming is similar to the one for forming glass or carbon based fabrics with similar yarn geometry. Different modes of deformation take place during forming. These are mainly in-plane shear, bending and tension of the reinforcement membrane. These loads are imposed at the same time on the material and are therefore coupled. This may favour the appearance of defects, depending on the shape complexity and the yarn architecture, as reported by Potter et al [171]. When flat yarns with aligned fibres are considered, defects such as tow buckles were reported to appear because of the yarn geometry, and also because of the high lateral stiffness conferred to the yarn by the addition of an adhesive (Fig.7). This is not specific to natural fibre based materials [172] but the phenomenon is increased if adhesives are used to bind natural fibre bundles together as it increases greatly the lateral stiffness of the yarn and therefore the bending angle at which the phenomenon takes place. A more specific defect associated with the use of textiles manufactured from finite length fibre bundles may happen during forming and was reported by Ouagne et al. [164]. Despite the use of adhesives, high strains were measured during forming [173]. These high strains are higher than the strain at which movements of bundles take place within the yarn under uniaxial or in bi-axial tension conditions [164]. The movements of packets of bundles were well reported by Moothoo et al [174]. They showed that local variations of fibre density take place. This is of course expected to be a source of inhomogeneity and therefore of weakness for the formed composite part. When adhesives are removed/washed after textile production, the strains observed during forming are even larger and therefore, the tensile resistance of the tows is low, and high strains may be observed in tows.

Solutions to prevent or to minimise the appearance of these specific defects have been proposed, and are based on various studies of this type of defect [165][166][175][176]. Solutions consist of adjusting the textile geometry [165] to remove the space where tow buckles take place, or by adjusting the forming device and particularly the blank-holder design to reduce the tension of the yarns associated with the high strains reported in the previous paragraph [166]. A complex tetragonal shape (Figure 13) without defect was obtained from a textile that was not specifically designed to prevent defects, by adjusting the forming process parameters and blank holder design. The extra challenge associated with the forming of textiles manufactured from natural fibre bundles was therefore met, and it was shown that with adequate materials and the appropriate process parameters it is possible to manufacture complex shape composite materials for load bearing applications with special designs manufactured from high capacity fibre bundles extracted from plants such as flax.

It is also possible to form non-woven fabrics [177] with relatively complex shapes such as hemispherical or corners. The main mechanism associated with non-woven textile forming is the movement of fibres within the fabric to accommodate the shape. In this case, variations of fibre density may be observed in high deformation zones. It is therefore important in this case to anticipate the density evolution in order to prevent the formation of zones with too low fibre densities, which could lead to weaknesses in composites.

Figure 13. Forming of complex shapes (a); Appearance of tow buckling (b)

4 / Manufacturing of biocomposites and associated properties

4.1 The main mechanisms controlling the final properties of manufactured structures.

Beyond their particular features, the choice of manufacturing process also has an important influence on the quality of the composite materials manufactured from plant fibres, and especially their mechanical properties.

As noted in the previous sections, there has been a large effort to understand the structure of plant fibres and to characterize fibre properties. However, this work is not easily transferred to composite materials as the manufacturing processes used in much of the published work are not optimized, so properties obtained can be far from optimal. The processes employed are generally those used for synthetic fibres, glass and carbon. However,

while these synthetic fibres can withstand the forming conditions this is not necessarily the case for plant fibres. It is therefore essential to define the allowable processing window for fibres such as flax.

Understanding, and hence optimization of the manufacturing process requires a rigorous description of the mechanisms which control the final component properties. Advanced physical and numerical models are being developed which attempt to account for all the coupled thermal, mechanical, and chemical effects, which contribute, to the final product. These can then be used to study the quality of the material through the different parameters, which affect properties. These include polymerization, crystallization, void development, fibre integrity, interface quality etc. A recent study by Cadu et al. [178] varied processing parameters of unidirectional flax reinforced epoxy during compression forming and showed the influence of seven process parameters on composite tensile properties. Fibre conditioning, pressure and temperature all affected the composite quality. Aslan et al [179] also highlighted the importance of consolidation pressure on the mechanical performance of flax/PET composites manufactured by press forming after winding.

Understanding plant fibre composites is part of a more general study of the behaviour of porous media made up of complex fibre entanglements. Continuous characterization of the structure of such materials and the elementary physico-chemical phenomena involved, from the nano-scale to full scale, is a major challenge in material science. The service conditions will dictate the choice of material, thermoset or thermoplastic, and the choice of fibre reinforcement, but it is the forming step which will create the fibre/matrix interfaces and determine the material quality. These interfaces produced during material consolidation can be differentiated from those present within the fibres themselves.

In section 3, the parameters which allow the mechanics of the pre-forming process to be controlled were described. In the following section the next step in the forming process, the hydrodynamics of polymer flow within the porous medium (reinforcement), and the thermo-kinetics imposed by the choice of polymer will be discussed. Particular attention will be given to the fibre surfaces and their treatment, as well as to the thermal and hygrothermal conditionning applied during composite manufacture.

4.2 / Flax fibre surfaces

If no aggressive surface treatment is applied, the surface of an elementary flax fibre corresponds to the primary cell wall. The thickness of this heterogeneous layer is around 200 nm [60]. It is composed of cellulose, hemicelluloses (mainly xuloglucan), and pectins (mainly homogalactorunan). Each of these three makes up about a third of the overall composition.
After retting, the more or less well-bonded remains of middle lamella can be found on individual fibres (Figure 14). These middle lamella keep the fibre bundles together and are composed of pectins (homogalacturonan and rhamnogalacturonan) [180]. This surface can be cleaned by chemical treatments (Figure 15). Such treatments will modify the surface composition, surface roughness, and fibre/matrix adhesion, but also the tensile properties of the fibres [181] [182].

Figure 14. Elementary Flax fibre after retting, showing remains of middle lamella on the surface [181]**.**

Figure 15. Elementary flax fibre after surface cleaning by a chemical treatment.

Figures 14 and 15 show kink bands on the fibres; this type of geometrical heterogeneity modifies the local stress distribution in the matrix within a composite [183].

4.3. Adhesion between plant fibres and polymers

The value usually employed to quantify the adhesion between a single fibre and a polymer is the interfacial shear strength. Several micro-mechanics tests are available such as fragmentation, micro-indentation, push-out, pull-out and micro-droplet debonding [184]. Each test has advantages and disadvantages and requires more or less input data. For example, a fragmentation test requires knowledge of the tensile strength of the fibres studied.

For plant fibres three types of test are commonly used: microdroplet debonding (microbond), pull-out and fragmentation [185]. Given the size of the specimens and the hypotheses made concerning the stress state, the value measured is an apparent interfacial shear strength. The difference in specimen geometries makes comparisons between values difficult. For example for the same batch of flax fibres and two polymers (PP and MAPP), Graupner et al. [185] applied pull-out and fragmentation tests (Table 1). While the use of a coupling agent (maleic anhydride) clearly leads to an increase in the shear strengths (by between 30% and 60%), the values from the two types of test are quite different (Table 1).

Table 1. Influence of the type of test on the measured apparent interfacial shear strength [185]**.**

Table 2 shows the apparent interfacial shear strength measured with the microdroplet test (Figure 16.A) in the same laboratory, under the same conditions and with the same test fixture [186][181][187][39][36][188]. The values were measured for glass and flax fibres with different polymers (thermoset and thermoplastic). Examination of Table 2 reveals that the values measured for glass fibres (with sizings) are generally higher than those for untreated flax fibres. The strength values for flax fibres are quite high; the interface does not appear to be a weak link even with a thermoplastic. An analysis of friction after debonding during this type of test (Figure 16. B) provides additional information on radial compression stresses. It is also possible to measure a wetting angle when liquid polymers are placed on fibres.

Table 2. Apparent interfacial shear strengths (IFSS) measured by the microdroplet test. All tests performed in the same laboratory with the same test fixture.

Figure 16. (Left) Schematic diagram of microdroplet test [190], (Right) Typical debonding behaviour [192]

Some additional remarks may be made:

- The nature of the batch of flax fibres (variety, growth conditions, retting quality, conditions of mechanical extraction of fibre bundles…) influences both the mechanical properties of the fibres and their surface state, and thus the fibre/matrix interface. When all other parameters are kept constant (same epoxy matrix, same manufacturing conditions and storage, same test fixture, operator, same mechanical behaviour …), the apparent interfacial shear strength varies with the type of fibre, going from 22.5 ± 1.5 MPa for a batch of Hermes fibres to 13.2 ± 3.2 MPa for a batch of Electra fibres. Of course, the difference between two batches of fibres is not limited to the flax variety [189] and the term 'flax' is thus inadequate; it is necessary to provide all available information on the batch.
- The type of matrix also requires a more detailed description. Marrot et al. [188] compared, with the same batch of flax, 5 different epoxy resins (partially biobased or not). The mean interfacial shear strength varied from 11.9 ± 4.1 MPa to 28.5 ± 6.4 MPa.
- For a semi-crystalline thermoplastic matrix such as PLA, the cooling rate has a strong influence on interfacial shear strengths [190]. The mean value increases as the cooling rate decreases (between 15.3 ±3.3 for air cooling and 22.2 ± 3.4 MPa for cooling at 1°C/min). This difference is due to thermally induced residual stresses.
- Although not always observed, in some industrial PP's flax fibres can act as nucleating agents [191] [191]. The presence of a transcrystalline zone around fibres is unfavorable for fibre/matrix adhesion [192].
- For an epoxy resin, the thermal cycle required to attain a proper degree of crosslinking can also affect the adhesion and the matrix properties, as shown for glass/epoxy fibre bundles [193].
- During debonding it is possible in some cases to see fibre outer wall peeling [194] . In this case the notion of interface must be questioned, as the flax fibre is itself a stack of layers reinforced by cellulose fibrils involving many interfaces which must be considered [195] and not only the interface between the polymer and the outer fibre layer.
- In some cases, with low viscosity resins, penetration of the matrix inside the fibre can be observed over a distance of around 1.5 µm, so once again the notion of interface becomes unclear. In this case the interface

becomes a complex interphase, within which an understanding of the biochemical composition of the cell walls becomes essential [189]. This observation has also been made for wood [196]. For flax fibres the impregnation by a melamine formaldehyde (MF) allows an increase in compression strength of the composite, but a drop in tension [197].

4.4. Fibre treatments

Treatments of different types have been tested on natural fibres in order to modify their chemical composition, especially surface properties. In particular, the main aim of these treatments is to modify the ratio between cellulose, hemicelluloses, pectins and lignin. The amount of lignin in flax fibres is low, the exact level depends on the maturity of the plant when it is uprooted [62]. It is known that pectins, lignin and hemicelluloses can be degraded or dissolved by acid and alkaline treatments [181] [198][199]. This can be used to estimate the relative content of these components in any kind of natural fibres, but also to modify their chemical structure and surface properties. Numerous studies have focused on the effect of an alkaline treatment on natural fibres. Some of these have combined an acid treatment with an alkaline one. In order to limit the environmental impact of these treatments, bio-based acids, such as formic acid, have been tested. Sizing inspired from those used for petro-sourced reinforcements have also been used. For example thermoplastic sizing on natural fibres has been explored. The following examples will focus on flax fibres since treatments have been more widely documented on those fibres. A last example of treatment that can modify the bonding properties of natural fibres with polymer matrix is plasma treatment under air or argon. Both atmospheric conditions and the plasma power appear to have an influence on natural fibre surface modification.

Alkaline treatments, the most common ones, aim to partially dissolve non-cellulosic polymers, such as pectins and hemicelluloses. Since mechanical properties are supposed to be mainly due to cellulose, this kind of treatment should remove additional complex components without modifying the mechanical behavior of fibres. Typical alkaline treatments can be an immersion in a sodium hydroxide (10g/L) ethanol solution for 2 hours at 78°C [181] or in a 1.5M sodium hydroxide solution for 1 hour at 100°C [199][200]. Alkaline treatments, even if they have been widely used in literature, have been found to have a very small effect on surface energy modification (the change is lower than 5% of the overall surface energy [181]). The polar component of the surface energy is slightly weakened, thus so is the total surface tension. Microbonding tests have shown that the shear strength and the critical rupture energy are lowered by more than half after this treatment. In order to improve interfacial properties, immersion in an acid solution can be added, to completely remove the non-cellulosic polymers.

The alkaline treatments described above can be coupled with an immersion in acid solutions. A typical example is an immersion for 1 hour in pure acetic anhydride at room temperature [194] or for a total dissolution of the non-cellulosic polymers immersion for one hour in a 0.015 M HCL solution at 100°C [199][200]. The immersion in acetic anhydride, coupled with the alkaline extraction, enhances slightly the shear strength measured by microbonding tests, even if the modification of surface energy is not significant. There is also a significant effect on the critical rupture energy measured during this test (roughly multiplied by 1.5). This indicates that, even if the alkaline treatment can be harmful, its coupling with an acid dissolution can improve interfacial properties.

Formic acid treatment is of particular interest since this acid can be bio-based and it allows the treatment duration to be shorter. Indeed, an immersion for 40 minutes at room temperature in 99% formic acid has been shown to have the same effect as the previous treatment (NaOH + acetic anhydride) [181]. The environmental impact is then lower and the process is much easier since no heating is required.

Standard sizings such as those used on glass are also used for basalt fibres. The latter have a mainly polar surface energy that makes them difficult to wet with mostly dispersive resins or polymer. The same sizing as for glass has been used to make the surface of those fibres more dispersive. For example, organosilanes can be used, and also thermoplastic coatings. Organosilane treatments are now well known and provide very good surface regularity. The process for thermoplastic coating can be non-homogeneous along the fibre, as shown by Pucci et al. [201].

Flax reinforcements can be subjected to a thermal treatment under neutral atmosphere in order to degrade the hemicelluloses that are partly responsible for the hydrophilic character of flax fibres. It has been shown on wood products [202][203] that hemicelluloses start to degrade at approximatively 200°C producing free radicals that are

susceptible to create cross-linking in lignins or pectins. Treated flax fibres have thus been subjected, after drying, to a temperature of 220°C for 2 h under circulation of nitrogen to prevent oxidation and fire [200][204][205]. Previous research on wood [202][203] has shown that the thermal treatment induces a degradation of hemicellulose. This degradation tends to produce free radicals that are by definition very unstable. Those free radicals tend to create cross-linking in lignins when they are generated in wood. Flax fibres contain a very low amount of lignin [206] and the measured amount of lignin can depend on the extraction method [206]. The process of free radical stabilization could thus be different. The difference in mass loss during selective dissolution [200] shows an effect of these free radicals on pectins. This may indicate an increase of the amount of structural pectins (the overall pectins are classified in structural and matrix pectins, this implies that a part of the matrix pectins have been converted into effective structural pectins that are more strongly bonded).

Recent studies have proven the positive effect of this kind of treatment on the surface energy of flax fibres [205] and thus on the impregnation by mostly dispersive resins, but also on swelling of those same fibres [207]. Thermal treatment under neutral atmosphere enhances the morphological stability of fibres and allows a more regular interface with a thermoset resin [207][205].

Finally, atmospheric plasma can be used to modify fibres. Plasma is usually generated between two electrodes through which runs an alternative current that creates a plasma in the selected operating gas. Gases used can be argon, air or ethylene [208][209]. The plasma power can be modulated and values in the literature vary from 100 W to 400 W [208][209]. The main effect of this treatment appears to be the surface roughness modification on flax fibres. A rougher surface can induce a better mechanical coupling between fibres and matrix. Bozaci et al. [208] have shown that even if the tensile strength of elementary fibres decreases when the plasma power increases, the IFSS is significantly improved. Bonding properties being determinant for composites, a slight decrease in tensile strength of fibres along with a significant increase in the IFSS results in a tougher composite. However, the usefulness of the rare data available in the literature on plant fibre composites after treatment of fibres is limited, since optimal control of manufacturing has yet to be achieved.

The main issue to be faced in the near future is the reliability of treatments, as they can be quite inhomogeneous along the fibre. Moreover, there is very little information about the durability of treatment effects on surface properties, first during storage of a fabric made with those fibres, and then during the lifetime of the composite after processing. Most of these treatments have not reached the industrial level, so fibres and composite are tested just after preparation. It has been shown [210] that processing itself can modify fibres properties. So it has to be proved that the surface modification of those fibres lasts at least until fibre/matrix interface formation during the manufacturing process. Then the durability of bonding properties under composite service conditions must be evaluated. Little information is available on the bonding between natural fibres and matrix polymers under service conditions and especially in humid environments.

4.5. Changes in mechanical properties of fibres during processing

Temperature may have a significant impact on plant cell wall mechanical properties and biochemical composition, these two aspects being closely linked. Due to the low degradation temperature of the plant cell wall, high temperatures (>170°C) lead to a biochemical modification or degradation of the plant cell wall structure. Parietal components of plant fibres are mainly composed of cellulose, but also include non-cellulosic polymers such as pectins and hemicelluloses. Paris et al. [211], on spruce and pine samples, showed an evaporation of water and dehydration with slight depolymerisation, but no change of cellulose microfibrils between 35°C and 250°C; they also highlighted an overall degradation of all non-cellulosic polymers such as pectins, as well as a degeneration of the cellulose crystal structure above 250°C. Moreover, Zolfrank and Fromm [212], also on wood, demonstrated a degradation of polyoses and a disorientation of cellulose microfibrils away from the fibre axis in the range of 200°C-250°C. Thus, although cellulose is the main component of the cell walls and the one that gives them their exceptional performance, the most heat-sensitive and labile are hemicelluloses and pectins which are the first to be degraded; this degradation has a direct impact on the structure and performance of plant cell walls.

Various studies in the literature have highlighted the impact of temperature on the performance of cell walls, fibres or biocomposites. At the cell wall scale, the effect of a heat treatment has been highlighted on bamboo [213] or wood [214] by showing an increase in the indentation modulus but also in hardness; this phenomenon is generally explained by a phenomenon of crosslinking of lignin and xylane [215,216]. This mechanical behaviour has also been demonstrated after a recycling of biocomposites inducing a succession of thermal cycles. Wood cell walls also show

an increase in their stiffness over cycles [217]; on the other hand, flax cell walls show the opposite phenomenon with a decrease in indentation mechanical properties due to their low lignin content and the alteration of their polysaccharide matrix with thermal exposure. This behaviour has been confirmed during various studies on recycling [40,218].

At the single fibre scale, the impact of temperature has also been demonstrated. Baley et al. [219] showed a marked drop in the mechanical tensile performance of elementary flax fibres after a thermal cycle of 14h at 105°C, which corresponds to a conventional drying time. The same trend could be noted for 8 minutes at 190, 210 or 250°C [220], the drop being all the more marked with the rise in temperature. These conditions correspond to a process cycle when the fibres are used with a thermoplastic resin. Thus, in addition to the temperature parameter, time must also be taken into account and it is the total thermal energy received by the material that will condition the drop in the performance of the plant walls; a compromise between these two parameters needs to be found, in order to respect fibre integrity [221]. By altering the non-cellulosic polymers of the walls responsible for their mechanical behaviour, the thermal cycle induces a modification of the phenomena involved during mechanical loading.

Tensile behaviour (stress-strain curves) of elementary flax fibres can be classified as one of three types: TI (linear), TII (two distinct linear sections), TIII (one non-linear section followed by an increase in the tangent modulus) [24].

Thus, the slip between the micro fibrils allowing the loading of the latter is no longer correctly ensured, which translates into a more brittle behaviour and premature failure leading to a majority of type II or even type I behaviour and not the type III characteristic for virgin fibres [220,222].

When processing a thermoplastic biocomposite, choices must therefore be made when selecting not only the resin but also the process conditions, in order to reduce temperatures and exposure times as much as possible. During a comparative study, Doumbia et al. [221] highlighted the importance of the processing route on the residence time, the use of a twin screw extruder making it possible to reduce by approximately a factor of 15 compared to a mixture made by BUSS co-mixer. Thus, depending on the process route chosen, the mechanical performance of the reinforcement fibres may change significantly during the process. This can be taken into account by designers by modelling; results have indeed shown that by taking into account the real mechanical performance of flax fibres that have undergone a thermal cycle [40] it was possible to accurately predict the stiffness of the associated composites.

4.6. Impregnation in bio-based composites

When manufacturing bio-based composites there is a tendency to use the processes developed over the last four decades for more conventional composites; these include the forming of pre-impregnated materials [223] used in autoclave-based processes or direct Liquid Composites Molding techniques [224]. In both routes, the impregnation of the fibre network is the key to successful manufacturing, leading to optimal properties of the final parts [225]. Controlling impregnation starts by mastering the intimate mechanisms of transient liquid-solid contact at the constituent level; at a higher scale, this will determine the wetting of the fibre network by resins. This is controlled by capillary effects at the fibre-resin scale, which in turn translate into permeability at the preform and part scales.

From the processing point of view, both the geometry and physico-chemical nature of fibres are of primary concern for bio-based composites. It may be noted that basalt fibres, which are derived from minerals but are in shape and nature very close to glass fibres, will behave very similarly to petro-sourced reinforcements based on carbon, glass, or aramid fibres [205]. Conversely, long fibres coming from crops like flax fibres, behave very differently regarding their particular fibre architecture and nature as described previously. Therefore, additional effects must be accounted for during the resin (liquid) impregnation of the flax fibre network [226,227].

Disregarding any sizing effect which is of little concern for flax fibres, the wetting, flows, and permeabilities involved in processing must account, above all, for the fibre swelling due to the capacity of natural fibres to absorb liquid components in their internal structure [205,228,229]. This swelling can be observed at several scales and has a strong influence on the final part properties due to internal stresses induced by the hygro-mechanical mismatch of the fibre-matrix behavior, as described earlier in this paper. Similar trends can be observed when internal thermo-chemo-mechanical stresses are built in petro-based composites [230,231]. As described earlier in this paper, this hydrophilic response can be reduced by appropriate surface treatments. In the case of the thermal treatment

proposed by Liotier and co-workers [200,204,205,232], this proved to modify significantly the wetting dynamics on individual fibres [205], and in turn to improve the wetting dynamics in flax fibre reinforcements [200,204], and consequently induced better mechanical properties of the manufactured parts [200,205].

At the fibre scale, Pucci *et al.* [205] characterised the local wetting dynamics on individual flax fibres accounting for fibre swelling. The wetted length (fibre perimeter) was characterised by both optical and tensiometric methods, before and after the wetting tests. They then showed that the swelling of the fibre modifies the wetting dynamics. Indeed, it was verified that the single mean advancing static contact angle, extracted through an original linear regression method applied on a whole set of fibres [233], decreased by 18% in water for instance.

At the scale of the preform, a common approach to composites processing consists of considering the preforms as porous equivalent orthotropic homogeneous media [234,235] where the fluid impregnation is usually described by the first gradient law of Darcy [236]. In that sense, the only characteristic of the preform is its permeability tensor. This 'simple' characteristic, in itself, hides all the complexity of the multi-scale flows in composites [237,238], and has been very widely studied, for both in-plane [239–242], transverse permeabilities [243,244] and 3D flows [245,246], and in both stationary [247–249] and transient regimes [250–252] and is still an active field of experimental research [242,250] and numerical modelling [253–255]. Some intermediate numerical approaches investigate the effects of the fluid-fibre affinity across scales [256] in order to avoid complex and expensive experiments. They can be dedicated to the investigation of the effects of flow regimes which control the void formation and convection in LCM processes for instance [257–260], including in dual-scale architectures [257,261,262]. They can also aim at defining equivalent properties such as capillary pressures which are induced by resin flow in fabrics due to capillary effects [263–265] and can be input in process simulations [234,266].

All these studies have focussed for a long time on petro-based high-performance composites, mainly due to the extensive use of these composites in aeronautics industry but also due to the lack of knowledge about the wetting mechanisms in flax fibres and preforms. More recently, a few permeability characterizations have been proposed for bio-based composites, and these revealed the effect of the fibre swelling at the preform scale in wetting liquids [267]. This was more clearly established at a lower scale in [200,204] by comparing wicking tests carried out in two preform types, made up respectively of (genuine) flax fibres and flax fibres treated to make them – almost-insensitive to swelling. As it can be verified, with water the response is non-linear (*Figure 1*7.A) while it remains linear with a non-wetting liquid (totally dispersive) like n-hexane. The only modification which can appear with water is then swelling. It was shown that this difference in mass uptake can be reproduced by Washburn's theory [268], modified to account for the fibre swelling, and yielding a contact angle even in this non-linear regime (*Figure 1*7.B).

Figure 17. Squared mass intake over time in wicking tests for quasi-UD at 35% fibre volume fraction - fibre direction - for (a) untreated and treated flax preforms, and (b) untreated flax preform fitted with a non-linear Washburn's modified theory accounting for swelling with the corresponding advancing contact angle identified through this model; from [204]

Going further on permeability measurements for flax long fibres, both saturated [269][267] and transient regimes [270] have been considered. Once again, it was shown that fibre swelling controls the non-Darcy type response of such fabrics. Accordingly, Park and co-workers have proposed a new resin flow model including the volumetric changes of resin and of fibre [227] as well as the permeability change due to the fibre swelling [267] which compares well with experiments. Following the developments in fabric forming prior to resin impregnation for petro-based composites [271,272], permeabilities in sheared flax fabrics have received very little attention, but these may be of primary importance [273].

Overall, the difficulties met in manufacturing petro-based composites are also encountered in long natural fibres, with additional difficulties due to the swelling of the fibres and fibre morphology during the impregnation stage. However, the work achieved on standard composites can be profitable for bio-based composites, provided the fibre sensitivity to swelling under hygroscopic conditions can be controlled or avoided.

4.7. Types of process

Having described the different coupled thermal/hygrothermal and mechanical loading conditions which composites are subjected to during manufacturing, this final section will provide a critical analysis of the choice of process technology. If biocomposites are to be produced correctly, it is important to propose appropriate manufacturing technology.

In general, the choice of process is mainly dependent on the shape of the component to be produced, the type of matrix, and the fibre aspect ratio. Table 3 summarizes the different manufacturing options, the selection criteria, and the associated coupled multiphysical parameters.

The shape of the component can be : i) profiled, high aspect ratio, ii) axisymmetric, iii) 3D (without a press) using a mould, iv) 3D without a press, with two moulds, v) 3D using a press, with two moulds. Table 3 shows the forming technologies for these shapes.

Table 3. Composite manufacturing processes.

AM[1] : Additive Manufacturing. AFP[2] : Automated Fiber Placement. ATL[3] : Automated Tape Laying. LRI[4] : Liquid Resin Infusion. RFI[5] : Resin Film Infusion. RTM[6] : Resin Transfer Molding. CRTM[7] : Compression Resin Transfer Molding

Concerning the choice of polymer, these are either liquid at room temperature and solidify at the processing temperature (thermoset) or in the form of compounds, film, powder or fibre at room temperature and become viscous at process temperature (thermoplastic). The fibre/matrix interface is created during the forming step. The main current research is devoted to new formulations of filled polymers (short fibres, particles, nano-fillers), thermoplastics, commingled polymers and more recently biosourced polymers with reduced VOC emissions. There are various semi-products for thermoplastic composites [282]: (a) pre-impregnated tow; (b) film; (c) powder-impregnated fibre bundle; (d) sheath-coated powder-impregnated fibre bundle; (e) non-commingled yarn; and (d) commingled yarn.

The final composite properties also depend on the fibre aspect ratio (length/diameter). A critical aspect ratio can be defined for particular loading conditions, so it is important to understand how the process selected will modify the aspect ratio.

The process can be defined according to the aspect ratio, with respect to the hydrodynamics of the liquid polymer flow. For short fibres and particles or nano-particles (L/d = 1-100), there is little relative movement, as in injection moulding or extrusion, or flow at the scale of a few fibres or particles (compression moulding). For long fibres (L/d > 1000), three cases can be considered: i) low relative flow rate (autoclave manufacture, AFP), ii) flow through the fibre bundle (pultrusion, filament winding, GMT, SMC,…), iii) flow in dual-scale fibrous porous medium (LCM Liquid Composite Molding: RTM, LRI …).

Going beyond these macroscopic scale definitions there is work underway to understand the mechanisms of impregnation (permeability) and fibre wetting, which requires a detailed investigation of the physico-chemical characteristics of fibre surfaces and their relation to geometrical and chemical heterogeneities (as described in sections 4.2, 4.3, 4.4, 4.6).

There is a wide range of plant fibre semi-products on the market: woven, braided, knitted preforms, SMC, prepreg, commingled, tape. The discontinuous nature of plant fibres requires special care during preform preparation. Current work is aimed at characterization of the elongation, shear, compaction and distortion of fibre bundles during forming and investigation of the friction between them (as described in section 3).

Most of the processes described above involve elevated temperatures. First, it is essential to control the humidity of plant fibre reinforcements, in order to reduce the appearance of defects. Then, much published work has focussed on thermal aspects, and particularly the changes in polymer microstructure (polymerization, crystallization), thermal exchange with the mould materials and with the reinforcement. During impregnation a complex material develops, made up of fully and partially saturated reinforcements together with dry reinforcement. The different heating techniques available (infrared, laser, oven, induction, resistance heating …) each have their own characteristics. The effects of temperature exposure on mechanical properties (see section 4.5) must also be understood. Using plant fibres will thus affect the heating and cooling technology choices.

With respect to the role of moisture, various results are available : the influence of drying fibres before impregnation of unidirectional plies was described in [219], the effects of moisture conditions during fibre conditioning on interfacial strength are discussed in [274], and the influence of post-cure temperature on composite properties is discribed in [275].

Finally, the choice of manufacturing technology must also consider energy requirements. The adoption of these bio-sourced materials in order to reduce environmental impact must also pay careful attention to selecting processes which respect the environment and, where possible, to reducing energy needs.

An approach which guarantees traceability at each step of the manufacturing process will allow a better understanding of the key parameters but also improve the credibility of the use of these materials.

Based on Table 3 it is hoped that a critical assessment of manufacturing methods can be made, resulting in adapting the process to these plant fibre composites and developing new processes, rather than attempting to adapt the material to traditional forming methods. Optimal composite properties can only be achieved when a thorough understanding of the multi-physical coupling between forming parameters exists.

5 / Conclusion

The aim of this review paper is to present the current status of the manufacturing of polymers reinforced by flax fibres, highlighting the specific nature of these reinforcements with respect to traditional fibres.

It was written following the realization that in many published papers on biocomposites the materials studied showed high void content levels and highly heterogeneous meso-structure. This can be explained by the lack of maturity, both of available preforms and of the particular behaviour of flax fibres during processing.

The first part of the review describes the context of biocomposite development. These fibres show good specific mechanical properties, long fibres, availability in Europe, and the existence of an industrial supply chain (from seed selection through to industrial extraction equipment). The renewable source of these fibres is also an essential element in life cycle analysis.

The complete fibre cycle, from plant to extraction, is discussed. In the plant the fibres are assembled in bundles, a retting step is needed to help separate the fibres during before extraction by mechanical scutching, and both steps affect the physical and mechanical properties of fibres.

The fibre length in the plant is quite short so it is necessary to create a reinforcement architecture which allows them to be impregnated. The textile solution of twisted fibre bundles can be used for flax fibres but has limitations due to the highly anisotropic fibre properties and impregnation difficulties. Other approaches have been developed, in particular the use of adhesives, and these are discussed. Overall, compared to synthetic fibres, the use of flax as a reinforcement requires a modified approach to preparing the reinforcement architecture.

The fourth section describes the forming process, with discussion on the fibre surface, fibre treatments, impregnation by polymers, and the different processes available. While most traditional composite forming processes can be applied to flax fibre reinforcements, the specific nature of the fibres requires care in selecting forming parameters. Improved understanding of this specific nature should lead to improved processing and hence to more optimal composite properties.

Acknowledgements

The authors are grateful to the CNRS for supporting the Research Group GDR 3671 (Mise en œuvre des matériaux composites et propriétés induites).

Compliance with Ethical Standards:

The authors declare that they have no conflict of interest.

References

[1] Naslain R. Introduction aux Matériaux Composites, n°2,. Edition du CNRS; 1985.

[2] Garvie RC, Hannink RH, Pascoe RT. Ceramic steel? Nature 1975;258:703–4.

[3] Porter DL, Heuer AH. Mechanisms of Toughening Partially Stabilized Zirconia (PSZ). J Am Ceram Soc 1977;60:183–4.

[4] Claussen N. Fracture Toughness of Al2O3 with an Unstabilized ZrO2Dispersed Phase. J Am Ceram Soc 1976;59:49–51.

[5] Ruf H, Evans AG. Toughening by Monoclinic Zirconia. J Am Ceram Soc n.d.;66:328–32. doi:10.1111/j.1151-2916.1983.tb10042.x.

[6] Faber KT, Evans GA. Intergranular Crack-Deflection Toughening in Silicon Carbide. J Am Ceram Soc 1983;66:C-94-C-95. doi:10.1111/j.1151-2916.1983.tb10084.x.

[7] Swain MV, Hannink RHJ, Garvie RC. Influence of precipitate size and temperature on the fracture toughness of calcia- and magnesia-partially stabilized zirconia. Fract Mech Ceram 1983;6:339–54.

[8] Evans AG, Cannon RM. Toughening of brittle solids by martensitic transformations. Acta Met 1986;34:761.

[9] Weibull W. A statistical distribution function of wide applicability. J Appl Mech 1951;18:293–7.

[10] Jayatilaka ADS. Fracture of Engineering Brittle Materials. Applied Science Publ. Ltd, London; 1979.

[11] Green, D J, Lange FF, James MR. Factors Influencing Residual Surface Stresses due to a Stress-Induced Phase Bansformation. J Am Ceram Soc n.d.;66:623–9. doi:10.1111/j.1151-2916.1983.tb10610.x.

[12] Becher PF, Ogle JC, Tiegs TN, Warwick WH. Toughening of ceramics by whisker reinforcement. Fract Mech Ceram 1986;7:61–74.

[13] Claussen N. Strengthening Strategies for ZrO2-Toughened Ceramics at High Temperatures. Mater Sci Eng 1986;71:23–38.

[14] Homeny J, Vaughn WL, Ferber MK. Processing and Mechanical Properties of SiC-Whisker-Al2O3-Matrix Composites. Am Ceram Soc Bull 1987;66:333–8.

[15] Faber KT, Evans AG. Crack deflection processes—I. Theory. Acta Metall 1983;31:565–76. doi:https://doi.org/10.1016/0001-6160(83)90046-9.

[16] Faber KT, Evans AG. Crack deflection processes—II. Experiment. Acta Metall 1983;31:577–84. doi:https://doi.org/10.1016/0001-6160(83)90047-0.

[17] Aveston J, Cooper MG, Kelly A. The properties of fibers composites. Conf. Proc. Natl. Phys. Lab. Teddington, UK, London , IPC Science and Technology Press Ltd.; 1971, p. 15–24.

[18] Bourmaud A, Beaugrand J, Shah DU, Placet V, Baley C. Towards the design of high-performance plant fibre composites. Prog Mater Sci 2018;97:347–408. doi:10.1016/j.pmatsci.2018.05.005.

[19] Eder M, Burgert I. Natural Fibres – Function in Nature Chapitre 2.2. Industrial. Wiley; 2010.

[20] van Dam JEG, Gorshkova TA. Fiber Formation. Encycl. Appl. Plant Sci., Elsevier; 2003, p. 87–96. doi:10.1016/B0-12-227050-9/00046-6.

[21] Baley C, Goudenhooft C, Gibaud M, Bourmaud A. Flax stems: from a specific architecture to an instructive model for bioinspired composite structures. Bioinspiration and Biomimetics 2018;13:12. doi:10.1088/1748-3190/aaa6b7.

[22] Baley C, Bourmaud A. Average tensile properties of French elementary flax fibers. Mater Lett 2014;122:159–61. doi:10.1016/j.matlet.2014.02.030.

[23] Baley C. Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase. Compos - Part A Appl Sci Manuf 2002;33:939–48. doi:10.1016/S1359-835X(02)00040-4.

[24] Lefeuvre A, Bourmaud A, Morvan C, Baley C. Elementary flax fibre tensile properties: Correlation between stress–strain behaviour and fibre composition. Ind Crops Prod 2014;52:762–9. doi:10.1016/j.indcrop.2013.11.043.

[25] Bourmaud A, Morvan C, Bouali A, Placet V, Perré P, Baley C. Relationships between micro-fibrillar angle, mechanical properties and biochemical composition of flax fibers. Ind Crops Prod 2013;44:343–51. doi:10.1016/j.indcrop.2012.11.031.

[26] Köhler L, Spatz H-C. Micromechanics of plant tissues beyond the linear-elastic range. Planta 2002;215:33–40. doi:10.1007/s00425-001-0718-9.

[27] Spatz H, Kohler L, Niklas KJ. Mechanical behaviour of plant tissues: composite materials or structures? J Exp Biol 1999;202:3269–72.

[28] Keryvin V, Lan M, Bourmaud A, Parenteau T, Charleux L, Baley C. Analysis of flax fibres viscoelastic behaviour at micro and nano scales. Compos Part A Appl Sci Manuf 2015;68. doi:10.1016/j.compositesa.2014.10.006.

[29] Lefeuvre A, Bourmaud A, Lebrun L, Morvan C, Baley C. A study of the yearly reproducibility of flax fiber tensile properties. Ind Crops Prod 2013;50:400–7. doi:10.1016/j.indcrop.2013.07.035.

[30] Baley C, Perrot Y, Busnel F, Guezenoc H, Davies P. Transverse tensile behaviour of unidirectional plies reinforced with flax fibres. Mater Lett 2006;60:2984–7. doi:10.1016/j.matlet.2006.02.028.

[31] Baley C, Kervoëlen A, Le Duigou A, Goudenhooft C, Bourmaud A. Is the low shear modulus of flax fibres an advantage for polymer reinforcement? Mater Lett 2016;185:534–6. doi:10.1016/j.matlet.2016.09.067.

[32] Scida D, Bourmaud B, Baley C, Bourmaud A, Baley C. Influence of the scattering of flax fibres properties for the calculation of flax/epoxy woven ply stiffness. Mater Des 2017;122:136–45. doi:10.1016/j.matdes.2017.02.094.

[33] Le Gall M, Davies P, Martin N, Baley C. Recommended flax fibre density values for composite property predictions. Ind Crops Prod 2018;114:52–8. doi:10.1016/j.indcrop.2018.01.065.

[34] Amiri A, Triplett Z, Moreira A, Brezinka N, Alcock M, Ulven CA. Standard density measurement method development for flax fiber. Ind Crops Prod 2017;96:196–202. doi:10.1016/j.indcrop.2016.11.060.

[35] Piggott MR. Mesostructures and their mechanics in fibre composites. Adv Compos Mater 1996;6:75–81.

[36] Coroller G, Lefeuvre A, Le Duigou A, Bourmaud A, Ausias G, Gaudry T, et al. Effect of flax fibres individualisation on tensile failure of flax/epoxy unidirectional composite. Compos Part A Appl Sci Manuf 2013;51:62–70. doi:10.1016/j.compositesa.2013.03.018.

[37] Bensadoun F, Verpoest I, Baets J, Müssig J, Graupner N, Davies P, et al. Impregnated Fibre Bundle Test for Natural Fibres used in Composites. J Reinf Plast Compos 2017;36:942–57. doi:10.1177/0731684417695461.

[38] Ouagne P, Bizet L, Baley C, Breard J, Bréard J, Breard J. Analysis of the Film-stacking Processing Parameters for PLLA/Flax Fiber Biocomposites. J Compos Mater 2010;44:1201–15. doi:10.1177/0021998309349019.

[39] Le Duigou A, Davies P, Baley C. Macroscopic analysis of interfacial properties of flax/PLLA biocomposites. Compos Sci Technol 2010;70:1612–20. doi:10.1016/j.compscitech.2010.06.001.

[40] Gourier C, Bourmaud A, Le Duigou A, Baley C. Influence of PA11 and PP thermoplastic polymers on recycling stability of unidirectional flax fibre reinforced biocomposites. Polym Degrad Stab 2017;136:1–9. doi:10.1016/j.polymdegradstab.2016.12.003.

[41] Baley C, Kervoëlen A, Lan M, Cartié D, Le Duigou A, Bourmaud A, et al. Flax/PP manufacture by automated fibre placement (AFP). Mater Des 2016;94:207–13. doi:10.1016/j.matdes.2016.01.011.

[42] Merotte J, Le Duigou A, Bourmaud A, Behlouli K, Baley C. Mechanical and acoustic behaviour of porosity controlled randomly dispersed flax/PP biocomposite. Polym Test 2016;51:174–80. doi:10.1016/j.polymertesting.2016.03.002.

[43] Baets J, Plastria D, Ivens I, Verpoest I. Determination of the optimal flax fibre preparation for use in unidirectional flax–epoxy composites. J Reinf Plast Compos 2014;33:493–505.

[44] Shah DU, Schubel PJ, Licence P, Clifford MJ. Determining the minimum, critical and maximum fibre content for twisted yarn reinforced plant fibre composites. Compos Sci Technol 2012;72:1909–17. doi:10.1016/j.compscitech.2012.08.005.

[45] Liang S, Gning P-B, Guillaumat L. Quasi-static behaviour and damage assessment of flax/epoxy composites. Mater Des 2015;67:344–53. doi:10.1016/j.matdes.2014.11.048.

[46] Liang S, Gning PB, Guillaumat L. A comparative study of fatigue behaviour of flax/epoxy and glass/epoxy composites. Compos Sci Technol 2012;72:535–43. doi:10.1016/j.compscitech.2012.01.011.

[47] Berges M, Léger R, Placet V, Person V, Corn S, Gabrion X, et al. Influence of moisture uptake on the static, cyclic and dynamic behaviour of unidirectional flax fibre-reinforced epoxy laminates. Compos Part A Appl Sci Manuf 2016;88:165–77. doi:10.1016/j.compositesa.2016.05.029.

[48] Acera Fernández J, Le Moigne N, Caro-Bretelle AS, El Hage R, Le Duc A, Lozachmeur M, et al. Role of flax cell wall components on the microstructure and transverse mechanical behaviour of flax fabrics reinforced epoxy biocomposites. Ind Crops Prod 2016;85:93–108. doi:10.1016/j.indcrop.2016.02.047.

[49] Poilâne C, Cherif ZE, Richard F, Vivet A, Ben Doudou B, Chen J. Polymer reinforced by flax fibres as a viscoelastoplastic material. Compos Struct 2014;112:100–12. doi:10.1016/j.compstruct.2014.01.043.

[50] Cherif ZE, Poil?ne C, Vivet A, Ben Doudou B, Chen J. About optimal architecture of plant fibre textile composite for mechanical and sorption properties. Compos Struct 2016;140:240–51. doi:10.1016/j.compstruct.2015.12.030.

[51] Santamala H, Livingston R, Sixta H, Hummel M, Skrifvars M, Saarela O. Advantages of regenerated cellulose fibres as compared to flax fibres in the processability and mechanical performance of thermoset composites. Compos Part A Appl Sci Manuf 2016;84:377–85. doi:10.1016/j.compositesa.2016.02.011.

[52] Liang S, Nouri H, Lafranche E. Thermo-compression forming of flax fibre-reinforced polyamide 6 composites: influence of the fibre thermal degradation on mechanical properties. J Mater Sci 2015;50:7660–72. doi:10.1007/s10853-015-9330-4.

[53] Baley C, Lan M, Bourmaud A, Duigou A Le, Le Duigou A. Compressive and tensile behaviour of unidirectional composites reinforced by natural fibres: Influence of fibres (flax and jute), matrix and fibre volume fraction. Mater Today Commun 2018;16:300–6. doi:https://doi.org/10.1016/j.mtcomm.2018.07.003.

[54] Gibaud M, Bourmaud A, Baley C. Understanding the lodging stability of green flax stems; The importance of morphology and fibre stiffness. Biosyst Eng 2015;137:9–21. doi:10.1016/j.biosystemseng.2015.06.005.

[55] Lefeuvre A, Bourmaud A, Baley C. Optimization of the mechanical performance of UD flax/epoxy composites by selection of fibres along the stem. Compos Part A Appl Sci Manuf 2015;77:204–8. doi:10.1016/j.compositesa.2015.07.009.

[56] Evert R. Esau's Plant Anatomy. Third Edition. John Wiley & Sons; 2006.

[57] Snegireva A V, Ageeva M V, Amenitskii SI, Chernova TE, Ebskamp M, Gorshkova TA. Intrusive growth of sclerenchyma fibers. Russ J Plant Physiol 2010;57:342–55. doi:10.1134/S1021443710030052.

[58] Ageeva M V, Petrovská B, Kieft H, Sal'nikov V V, Snegireva A V, van Dam JEG, et al. Intrusive growth of flax phloem fibers is of intercalary type. Planta 2005;222:565–74. doi:10.1007/s00425-005-1536-2.

[59] Gorshkova TA, Sal'nikov V V., Chemikosova SB, Ageeva M V., Pavlencheva N V., van Dam JEG. The snap point: a transition point in Linum usitatissimum bast fiber development. Ind Crops Prod 2003;18:213–21. doi:10.1016/S0926-6690(03)00043-8.

[60] Rihouey C, Paynel F, Gorshkova T, Morvan C. Flax cellulosic fibres: how to assess the non-cellulosic polysaccharides and to approach cell wall supramolecular design. Cellulose 2017;24:1985–2001.

[61] Goudenhooft C, Siniscalco D, Arnould O, Bourmaud A, Sire O, Gorshkova TT., et al. Investigation of the Mechanical Properties of Flax Cell Walls during Plant Development: The Relation between Performance and Cell Wall Structure. Fibers 2018;6:6. doi:10.3390/fib6010006.

[62] Bert F. Lin fibre—culture et transformation. Arvalis; 2013.

[63] Placet V, Day A, Beaugrand J. The influence of unintended field retting on the physicochemical and mechanical properties of industrial hemp bast fibres. J Mater Sci 2017;52:5759–77. doi:10.1007/s10853-017-0811-5.

[64] Djemiel C, Grec S, Hawkins S. Characterization of Bacterial and Fungal Community Dynamics by High-Throughput Sequencing (HTS) Metabarcoding during Flax Dew-Retting. Front Microbiol 2017;8:2052. doi:10.3389/fmicb.2017.02052.

[65] Meijer WJM, Vertregt N, Rutgers B, van de Waart M. The pectin content as a measure of the retting and rettability of flax. Ind Crops Prod 1995;4:273–84. doi:10.1016/0926-6690(95)00041-0.

[66] Sharma HSS, Faughey G, Lyons G. Comparison of physical, chemical, and thermal characteristics of water-, dew-, and enzyme-retted flax fibers. J Appl Polym Sci 1999;1:139–143.

[67] Martin N, Mouret N, Davies P, Baley C. Influence of the degree of retting of flax fibers on the tensile properties of single fibers and short fiber/polypropylene composites. Ind Crops Prod 2013;49:755–67. doi:10.1016/j.indcrop.2013.06.012.

[68] Van de Weyenberg I, Ivens J, De Coster A, Kino B, Baetens E, Verpoest I. Influence of processing and chemical treatment of flax fibres on their composites. Compos Sci Technol 2003;63:1241–6. doi:10.1016/S0266-3538(03)00093-9.

[69] Alix S, Lebrun L, Marais S, Philippe E, Bourmaud A, Baley C, et al. Pectinase treatments on technical fibres of flax: Effects on water sorption and mechanical properties. Carbohydr Polym 2012;87:177–85. doi:10.1016/j.carbpol.2011.07.035.

[70] Velde K Van de, Baetens E. Thermal and Mechanical Properties of Flax Fibres as Potential Composite Reinforcement. Macromol Mater Eng 2001;286:342–9.

[71] Pillin I, Kervoelen A, Bourmaud A, Goimard J, Montrelay N, Baley C. Could oleaginous flax fibers be used as reinforcement for polymers? Ind Crops Prod 2011;34:1556–63. doi:10.1016/j.indcrop.2011.05.016.

[72] Akin DE, Gamble GR, Morrison Iii WH, Rigsby LL, Dodd RB, Morrison I, et al. Chemical and Structural Analysis of Fibre and Core Tissues from Flax. J Sci Food Agric 1996;72:155–65. doi:10.1002/(sici)1097-0010(199610)72:2<155::aid-jsfa636>3.0.co;2-x.

[73] Pallesen BE. The quality of combine-harvested fibre flax for industrials purposes depends on the degree of retting. Ind Crops Prod 1996;5:65–78. doi:10.1016/0926-6690(95)00049-6.

[74] Mooney C, Stolle-Smits T, Schols H, de Jong E. Analysis of retted and non retted flax fibres by chemical and enzymatic means. J Biotechnol 2001;89:205–216.

[75] Segal L, Creely JJ, Martin AE, Conrad CM. An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. Text Res J 1959;29:786–94. doi:10.1177/004051755902901003.

[76] Zafeiropoulos NE, Baillie CA, Matthews FL. A study of transcrystallinity and its effect on the interface in flax fibre reinforced composite materials. Compos Part A Appl Sci Manuf 2001;32:525–43. doi:http://dx.doi.org/10.1016/S1359-835X(00)00058-0.

[77] Marrot L. Contribution au développement de matériaux composites à matrices thermodurcissables biosourcées et renforcées par des fibres végétales. University of South Brittany, 2014.

[78] Aslan M, Mehmood S, Madsen B, Goutianos S. The effect of processing on defects and tensile strength of single flax fibres. ECCM14, 2010.

[79] Baley C, Le Duigou A, Morvan C, Bourmaud A. Tensile properties of flax fibers. In: Bunsell AR, editor. Handb. Prop. Text. Tech. Fibres. Second Ed. Elsevier, 2018, p. 275–300. doi:10.1016/B978-0-08-101272-7.00008-0.

[80] Sultana C. Scutching of retted-flax straw. In: Sharma, H.S.S., Van Sumere CF, editor. Biol. Process. Flax., M Publications, Belfast, NorthernIreland.; 1992.

[81] Salmon-Minotte J. Flax. In: Franck, R.R. (Ed.), editor. Bast Other Plant Fibres., CRCPress, Woodhead Publishing, Cambridge.; 2005.

[82] Martin N, Davies P, Baley C. Comparison of the properties of scutched flax and flax tow for composite material reinforcement. Ind Crops Prod 2014;61:284–92. doi:10.1016/j.indcrop.2014.07.015.

[83] Goudenhooft C, Bourmaud A, Baley C. Varietal selection of flax over time: Evolution of plant architecture related to influence on the mechanical properties of fibers. Ind Crops Prod 2017;97:56–64. doi:10.1016/j.indcrop.2016.11.062.

[84] Lefeuvre A, Bourmaud A, Morvan C, Baley C. Tensile properties of elementary fibres of flax and glass: Analysis of reproducibility and scattering. Mater Lett 2014;130:289–91. doi:10.1016/j.matlet.2014.05.115.

[85] Bourmaud A, Gibaud M, Baley C. Impact of the seeding rate on flax stem stability and the mechanical properties of elementary fibres. Ind Crops Prod 2016;80:17–25. doi:10.1016/j.indcrop.2015.10.053.

[86] Barbulée A. Compréhension des effets du défibrage sur la morphologie, les propriétés et le comportement mécanique des faisceaux de fibres de lin. Etude d'un composite dérivé lin-époxyde. PhD dissertation at teh University of Caen in Lower Normandy, France., 2015.

[87] Decrette M, Mourad S, Osselin J., Drean J. Jacquard UNIVAL 100 parameters study for high-density weaving optimization. J Ind Text 2016;45:1603–18. doi:10.1177/1528083714567241.

[88] Tourlonias M, Bueno M. M-A, Ordan C, Poquillon D, Jordan C, Poquillon D. Influence of Wear on the Sizing Layer and Desizing of Single Carbon Fibre-to-Fibre Friction. Wear 2018;402–403:64–70. doi:10.1016/J.WEAR.2018.02.003.

[89] Ramachandran T, Gobi N, Rajendran V, Lakshmikantha C. Optimization of process parameters for crease resistant finishing of coton fabric using citric acid. Indian J Fibres Text Res 2009;34:359–67.

[90] Ameri E, Lebrun G, Laperrière L. In-plane permeability characterization of a unidirectional flax/paper reinforcement for liquid composite molding processes. Compos Part A Appl Sci Manuf 2016;85:52–64. doi:https://doi.org/10.1016/j.compositesa.2016.03.002.

[91] Habibi M, Laperrière L, Lebrun G, Chabot B. Experimental Investigation of the Effect of Short Flax Fibers on the Permeability Behavior of a New Unidirectional Flax/Paper Composite. Fibers 2016;4. doi:10.3390/fib4030022.

[92] Couture A, Lebrun G, Laperrière L. Mechanical properties of polylactic acid (PLA) composites reinforced with unidirectional flax and flax-paper layers. Compos Struct 2016;154:286–95. doi:https://doi.org/10.1016/j.compstruct.2016.07.069.

[93] Baghaei B, Skrifvars M, Berglin L. Manufacture and characterisation of thermoplastic composites made from PLA/hemp co-wrapped hybrid yarn prepregs. Compos Part A Appl Sci Manuf 2013;50:93–101. doi:10.1016/J.COMPOSITESA.2013.03.012.

[94] Goutianos S, Peijs T, Nystrom B, Skrifvars M. Development of Flax Fibre based Textile Reinforcements for Composite Applications. Appl Compos Mater 2006;13:199–215. doi:10.1007/s10443-006-9010-2.

[95] Shah D, Nag N, Clifford M. Why do we observe significant differences between measured and 'back-calculated' properties of natural fibres? Cellulose 2016;23:1481–90. doi:10.1007/s10570-016-0926-x.

[96] Shah DU. Damage in biocomposites: Stiffness evolution of aligned plant fibre composites during monotonic

and cyclic fatigue loading. Compos Part A Appl Sci Manuf 2016;83:160–8. doi:10.1016/j.compositesa.2015.09.008.

[97] Shah DU. Natural fibre composites: Comprehensive Ashby-type materials selection charts. Mater Des 2014;62:21–31. doi:10.1016/j.matdes.2014.05.002.

[98] Xue D, Miao M, Hu H. Permeability anisotropy of flax nonwoven mats in vacuum-assisted resin transfer molding. J Text Inst 2011;102:612–20. doi:10.1080/00405000.2010.504566.

[99] Das D. Introduction to composite nonwovens. In: Das D, Pourdeyhimi B, editors. Compos. nonwoven Mater. Struct. Prop. Appl., Cambridge, UK: Woodhead Publishing Series in Textiles: Number 155; 2014.

[100] Das D, Pradhan AK, Chattopadhyay R, Singh SN. Composite nonwovens. Text Prog 2012;44:1–84.

[101] INDA. INDA: Association of the Nonwoven Fabrics Industry. http://www.inda.org/. n.d.

[102] Mosca SM. Flax in nonwovens. Textilia 1986;62:29.

[103] Boettcher P, Schmalz E. Flax in nonwovens. Text Prax Int 1993;48:585.

[104] Maity S, Gon DP, Paul P. A Review of Flax Nonwovens: Manufacturing, Properties, and Applications. J Nat Fibers 2014;11:365–90. doi:10.1080/15440478.2013.861781.

[105] Moryganov AP, Galashina VN, Dymnikova NS, Stokozenko VG, Danilov AR. Modification of flax fibres: From research to realization. Fibre Chem 2008;40:234–40. doi:10.1007/s10692-008-9046-1.

[106] Ecotechnilin. Ecotechnilin. http://www.eco-technilin.com/activity-process.asp n.d.

[107] Merotte J, Le Duigou A, Kervoelen A, Bourmaud A, Behlouli K, Sire O, et al. Flax and hemp nonwoven composites: The contribution of interfacial bonding to improving tensile properties. Polym Test 2018;66:303–11. doi:10.1016/j.polymertesting.2018.01.019.

[108] Anandjiwala RD, Boguslavsky L. Development of Needle-punched Nonwoven Fabrics from Flax Fibers for Air Filtration Applications. Text Res J 2008;78:614–24. doi:10.1177/0040517507081837.

[109] Fages E, Gironés S, Sánchez-Nacher L, García-Sanoguera D, Balart R. Use of wet-laid techniques to form flax-polypropylene nonwovens as base substrates for eco-friendly composites by using hot-press molding. Polym Compos n.d.;33:253–61. doi:10.1002/pc.22147.

[110] Gnaba I, Omrani F, Wang P, Soulat D, Ferreira M, Vroman P, et al. Mechanical behavior of flax/polypropylene commingled nonwoven at dry scale: Influence of process parameters. Text Res J n.d.;0:0040517518755789. doi:10.1177/0040517518755789.

[111] Zhang L, Miao M. Commingled natural fibre/polypropylene wrap spun yarns for structured thermoplastic composites. Compos Sci Technol 2010;70:130–5. doi:10.1016/j.compscitech.2009.09.016.

[112] Jiang Z, Yu C, Yang J, Han G, Xing M. Estimation of yarn strength based on critical slipping length and fiber length distribution. Text Res J 2017;16. doi:10.1177/0040517517741160.

[113] Hearle J, Grosberg P, Backer S. Structural mechanics of fibers, yarns and fabrics. New York: Wiley-Interscience; 1969.

[114] Pan N. Development of a Constitutive Theory for Short Fiber Yarns: Mechanics of Staple Yarn Without Slippage Effect. Text Res J 1992;62:749–65. doi:10.1177/004051759206201208.

[115] Pan N. Development of a Constitutive Theory for Short Fiber Yarns Part II: Mechanics of Staple Yarn With Slippage Effect. Text Res J 1993;63:504–14. doi:10.1177/004051759306300902.

[116] Pan N. Development of a Constitutive Theory for Short Fiber Yams: Part III: Effects of Fiber Orientation and Bending Deformation. Text Res J 1993;63:565–72. doi:10.1177/004051759306301002.

[117] Frydrych I. A New Approach for Predicting Strength Properties of Yarn. Text Res J 1992;62:340–8. doi:10.1177/004051759206200606.

[118] Frydrych I. Relation of Single Fiber and Bundle Strengths of Cotton. Text Res J 1995;65:513–21. doi:10.1177/004051759506500905.

[119] Pan N. Prediction of statistical strengths of twisted fibre structures. J Mater Sci 1993;28:6107–14. doi:10.1007/BF00365030.

[120] Pan N, Hua T, Qiu Y. Relationship Between Fiber and Yarn Strength. Text Res J 2001;71:960–4. doi:10.1177/004051750107101105.

[121] Gregory J. Cotton yarn structure Part IV—The Strength of twisted yarn elements in relation to the properties of the constituents fibres. J Text Inst Trans 1953;44:T499–514. doi:10.1080/19447025308662613.

[122] Jiang Z, Hu Y, Kuang X, Yu C, Yang J. Simulation on fiber random arrangement in the yarn. J Text Inst 2014;105:1312–8. doi:10.1080/00405000.2014.891685.

[123] Yan G, Yu C. A joint influence of the distributions of fiber length and fineness on the strength efficiency of the fibers in yarn. Fibers Polym 2007;8:309–12. doi:10.1007/BF02877275.

[124] Omrani F, Wang P, Soulat D, Ferreira M. Mechanical properties of flax-fibre-reinforced preforms and composites: Influence of the type of yarns on multi-scale characterisations. Compos Part A Appl Sci Manuf 2017;93:72–81. doi:10.1016/J.COMPOSITESA.2016.11.013.

[125] Belaadi A, Bourchak M, Aouici H. Mechanical properties of vegetal yarn: Statistical approach. Compos Part B Eng 2016;106:139–53. doi:10.1016/J.COMPOSITESB.2016.09.033.

[126] Blanchard JMFA, Sobey AJJ, Blake JIRIR. Multi-scale investigation into the mechanical behaviour of flax in yarn, cloth and laminate form. Compos Part B Eng 2016;84:228–35. doi:https://doi.org/10.1016/j.compositesb.2015.08.086.

[127] Khalfallah M, Abbès B, Abbès F, Guo YQ, Marcel V, Duval A, et al. Innovative flax tapes reinforced Acrodur biocomposites: A new alternative for automotive applications. Mater Des 2014;64:116–26. doi:10.1016/j.matdes.2014.07.029.

[128] Shah DU, Schubel PJ, Clifford MJ. Modelling the effect of yarn twist on the tensile strength of unidirectional plant fibre yarn composites. J Compos Mater 2013;47:425–36. doi:10.1177/0021998312440737.

[129] Goutianos S, Peijs T. The optimization of flax fibre yarns for the development of high-performance natural fibre composites. Adv Compos Lett 2003;13:199–215.

[130] Dissanayake NPJ, Summerscales J, Grove SM, Singh MM. Energy Use in the Production of Flax Fiber for the Reinforcement of Composites. J Nat Fibers 2009;6:331–46. doi:10.1080/15440470903345784.

[131] Sicomin. http://www.sicomin.com/products/epoxy-systems/bio-based-epoxy n.d.

[132] Kuraray. https://www.kuraray.eu/fileadmin/Downloads/ELVANOL/ELVANOL_technical_data_sheets/Elvanol_R_T-66_DS_Kuraray_P2.pdf n.d.

[133] Avebe. www.avebe.com/textile-warp-sizing/ n.d.

[134] Suedstaerke. http://www.suedstaerke.de/index.php?Starches-for-the-textile-industry n.d.

[135] Imam SH, Bilbao-Sainz C, Chiou B-S, Glenn GM, Orts WJ. Biobased adhesives, gums, emulsions, and binders: current trends and future prospects. J Adhes Sci Technol 2013;27:1972–97. doi:10.1080/01694243.2012.696892.

[136] Britannica. https://www.britannica.com/technology/gum-adhesive n.d.

[137] Parija S, Misra M, Mohanty AK. STUDIES OF NATURAL GUM ADHESIVE EXTRACTS: AN OVERVIEW. J Macromol Sci Part C 2001;41:175–97. doi:10.1081/MC-100107775.

[138] Veluraja K, Ayyalnarayanasubburaj S, Paulraj AJ. Preparation of gum from Tamarind seed — and its application in the preparation of composite material with sisal fibre. Carbohydr Polym 1997;34:377–9.

doi:10.1016/S0144-8617(97)00128-8.

[139] Oswamani B, Ananjiwala R, Hall D. Textile Sizing. Marcel Dekker, Inc; 2004.

[140] Opwis K, Mayer-Gall T, Gutmann JS, Dammer C, Titscher T, Nickisch-Hartfiel A, et al. Semi-industrial production of methane from textile wastewaters. Energy Sustain Soc 2012;2:1–6. doi:10.1186/2192-0567-2-1.

[141] Kumar N, Das D. Fibrous biocomposites from nettle (Girardinia diversifolia) and poly(lactic acid) fibers for automotive dashboard panel application. Compos Part B Eng 2017;130:54–63. doi:https://doi.org/10.1016/j.compositesb.2017.07.059.

[142] Lawrence C. Advances in yarn spinning technology. Woodhead Publishing Series in Textiles; 2010.

[143] Gu H, Miao M. Optimising fibre alignment in twisted yarns for natural fibre composites. J Compos Mater 2014;48:2993–3002. doi:10.1177/0021998313504322.

[144] Bensadoun F, Vallons KAM, Lessard LB, Verpoest I, Van Vuure AW. Fatigue behaviour assessment of flax-epoxy composites. Compos Part A Appl Sci Manuf 2015;82:253–66. doi:10.1016/j.compositesa.2015.11.003.

[145] Bensadoun F. In-service behaviour of flax fibre reinforced composites for high performance applications. Phd-thesis of Faculty of Engineering Science, KU Leuven, 2016.

[146] Ma H, Li Y, Wang D. Investigations of fiber twist on the mechanical properties of sisal fiber yarns and their composites. J Reinf Plast Compos 2014;33:687–96. doi:10.1177/0731684413520187.

[147] Rask M, Madsen B. Twisting of fibres in yarns for natural fibre composites. ICCM18 – 18th Int. Conf. Compos. Mater. Jeju Island, Korea., 2011, p. 5.

[148] Lansiaux H, Corbin AC, Soulat D, Boussu F, Ferreira M, Labanieh AR. Identification du comportement mécanique de tissu 3D interlock chaine à base de mèches de lin. Journées Jeunes Cherch. en Ecocomposites Compos. Bio-sourcés. ENI-Tarbes, 2018.

[149] Xie Y, Oxenham W, Grosberg P. 24—A study of the strength of wrapped yarn part I: the theorical model. J Text Inst 1986;77:295–304. doi:10.1080/00405008608658424.

[150] Xie Y, Oxenham W, Grosberg P. 25—A study of the strength of wrapped yarns part II: computation and experimental. J Text Inst 1986;77:305–13. doi:10.1080/00405008608658425.

[151] Xie Y, Oxenham W, Grosberg P. 26—A study of the strength of wrapped yarns part III: The relationship between structural paraleters and strength. J Text Inst 1986;77:314–26. doi:10.1080/00405008608658426.

[152] Jiang J, Chen N. Preforms and composites manufactured by novel flax/polypropylene cowrap spinning method. J Compos Mater 2012;46:2097–109. doi:10.1177/0021998311430155.

[153] Khondker OA, Ishiaku US, Nakai A, Hamada H. A novel processing technique for thermoplastic manufacturing of unidirectional composites reinforced with jute yarns. Compos Part A Appl Sci Manuf 2006;37:2274–84. doi:10.1016/j.compositesa.2005.12.030.

[154] Jayaraman K. Manufacturing sisal–polypropylene composites with minimum fibre degradation. Compos Sci Technol 2003;63:367–74. doi:https://doi.org/10.1016/S0266-3538(02)00217-8.

[155] Kobayashi S, Takada K. Processing of unidirectional hemp fiber reinforced composites with micro-braiding technique. Compos Part A Appl Sci Manuf 2013;46:173–9. doi:https://doi.org/10.1016/j.compositesa.2012.11.012.

[156] Bar M, Das A, Alagirusamy R. Effect of interface on composites made from DREF spun hybrid yarn with low twisted core flax yarn. Compos Part A Appl Sci Manuf 2018;107:260–70. doi:https://doi.org/10.1016/j.compositesa.2018.01.003.

[157] Bar M, Das A, Alagirusamy R. Studies on flax-polypropylene based low-twist hybrid yarns for thermoplastic composite reinforcement. J Reinf Plast Compos 2017;36:818–31. doi:10.1177/0731684417693428.

[158] Alagirusamy R, Fangueiro R, Ogale V, Padaki N. Hybrid Yarns and Textile Preforming for Thermoplastic

Composites. Text Prog 2006;38:1–71. doi:10.1533/tepr.2006.0004.

[159] Selver E, Potluri, E. Selver PP. Glass/Polypropylene commingled yarns for damage tolerant thermoplastic composites. Eur Mech Sci 2017;1:93–103.

[160] Sathishkumar TP, Naveen J, Satheeshkumar S. Hybrid fiber reinforced polymer composites – a review. J Reinf Plast Compos 2014;33:454–71. doi:10.1177/0731684413516393.

[161] Wang P, Legrand X, Soulat D. Three-Dimentional Textile Preform Using Advanced Textile Technologies for Composite Manufacturing. In: Kumar B, editor. Text. Adv. Appl., Rijeka: InTech; 2017. doi:10.5772/intechopen.68175.

[162] Gommer F, Endruweit A, Long AC. Quantification of micro-scale variability in fibre bundles. Compos Part A Appl Sci Manuf 2016;87:131–7. doi:https://doi.org/10.1016/j.compositesa.2016.04.019.

[163] Misnon MI, Islam MM, Epaarachchi JA, Lau KT. Analyses of woven hemp fabric characteristics for composite reinforcement. Mater Des 2015;66:82–92. doi:https://doi.org/10.1016/j.matdes.2014.10.037.

[164] Ouagne P, Soulat D, Tephany C, Duriatti D, Allaoui S, Hivet G. Mechanical characterisation of flax-based woven fabrics and in situ measurements of tow tensile strain during the shape forming. J Compos Mater 2013;47:3501–15. doi:10.1177/0021998312467217.

[165] Ouagne P, Soulat D, Moothoo J, Capelle E, Gueret S. Complex shape forming of a flax woven fabric; analysis of the tow buckling and misalignment defect. Compos Part A Appl Sci Manuf 2013;51:1–10. doi:https://doi.org/10.1016/j.compositesa.2013.03.017.

[166] Capelle E, Ouagne P, Soulat D, Duriatti D. Complex shape forming of flax woven fabrics: Design of specific blank-holder shapes to prevent defects. Compos Part B Eng 2014;62:29–36. doi:https://doi.org/10.1016/j.compositesb.2014.02.007.

[167] Duc F, Bourban P-E, Månson J-AE. Dynamic mechanical properties of epoxy/flax fibre composites. J Reinf Plast Compos 2014;33:1625–33. doi:10.1177/0731684414539779.

[168] Xue D, Hu H. Mechanical properties of biaxial weft-knitted flax composites. Mater Des 2013;46:264–9. doi:https://doi.org/10.1016/j.matdes.2012.10.019.

[169] Jacquot P-B, Wang P, Soulat D, Legrand X. Analysis of the preforming behaviour of the braided and woven flax/polyamide fabrics. J Ind Text 2016;46:698–718. doi:10.1177/1528083715591592.

[170] Ouagne P, Soulat D, Hivet G, Duriatti D. Analysis of defects during the preforming of a woven flax reinforcement. Adv Compos Lett 2011;20:105–8.

[171] Potter K, Khan B, Wisnom M, Bell T, Stevens J. Variability, fibre waviness and misalignment in the determination of the properties of composite materials and structures. Compos Part A Appl Sci Manuf 2008;39:1343–54. doi:https://doi.org/10.1016/j.compositesa.2008.04.016.

[172] Allaoui S, Hivet G, Soulat D, Wendling A, Ouagne P, Chatel S. Experimental preforming of highly double curved shapes with a case corner using an interlock reinforcement. Int J Mater Form 2014;7:155–65. doi:10.1007/s12289-012-1116-5.

[173] Ouagne P, Soulat D, Tephany C, Moothoo J, Allaoui S, Hivet G, et al. Complex Shape Forming of Flax Based Woven Fabrics - Analysis of the Yarn Tensile Strain during the Process. Mater. Form. ESAFORM 2012, vol. 504, Trans Tech Publications; 2012, p. 231–6. doi:10.4028/www.scientific.net/KEM.504-506.231.

[174] Moothoo J, Allaoui S, Ouagne P, Soulat D. A study of the tensile behaviour of flax tows and their potential for composite processing. Mater Des 2014;55:764–72. doi:https://doi.org/10.1016/j.matdes.2013.10.048.

[175] Ouagne P, Soulat D, Tephany C, Gillibert J. Measurement of the Appearance and Growth of Tow Buckling Defect in the Frame of Complex Shape Manufacturing Process by Using Fringe Projection Technique. Strain 2016;52:559–69. doi:10.1111/str.12206.

[176] Tephany C, Gillibert J, Ouagne P, Hivet G, Allaoui S, Soulat D. Development of an experimental bench to

reproduce the tow buckling defect appearing during the complex shape forming of structural flax based woven composite reinforcements. Compos Part A Appl Sci Manuf 2016;81:22–33. doi:https://doi.org/10.1016/j.compositesa.2015.10.011.

[177] Omrani F, Wang P, Soulat D, Ferreira M, Ouagne P. Analysis of the deformability of flax-fibre nonwoven fabrics during manufacturing. Compos Part B Eng 2017;116:471–85. doi:https://doi.org/10.1016/j.compositesb.2016.11.003.

[178] Cadu T, Berges M, Sicot O, Person V, Piezel B, Van Schoors L, et al. What are the key parameters to produce a high-grade bio-based composite? Application to flax/epoxy UD laminates produced by thermocompression. Compos Part B Eng 2018;150:36–46. doi:10.1016/J.COMPOSITESB.2018.04.059.

[179] Aslan M, Mehmood S, Madsen B. Effect of consolidation pressure on volumetric composition and stiffness of unidirectional flax fibre composites. J Mater Sci 2013;48:3812–24. doi:10.1007/s10853-013-7182-3.

[180] Andème-Onzighi C, Girault R, His I, Morvan C, Driouich A. Immunocytochemical characterization of early-developing flax fiber cell walls. Protoplasma 2000;213:235–45. doi:10.1007/BF01282161.

[181] Baley C, Busnel F, Grohens Y, Sire O. Influence of chemical treatments on surface properties and adhesion of flax fibre–polyester resin. Compos Part A Appl Sci Manuf 2006;37:1626–37. doi:10.1016/j.compositesa.2005.10.014.

[182] Bismarck A, Aranberri-Askargorta I, Springer J, Lampke T, Wielage B, Stamboulis A, et al. Surface characterization of flax, hemp and cellulose fibers; Surface properties and the water uptake behavior. Polym Compos 2002;23:872–94.

[183] Hughes M, Sèbe G, Hague J, Hill C, Spear M, Mott L. An investigation into the effects of micro-compressive defects on interphase behaviour in hemp-epoxy composites using half-fringe photoelasticity. Compos Interfaces 2000;7:13–29. doi:10.1163/156855400300183551.

[184] Pitkethly M, Favre J, Gaur U, Jakubowski J, Mudrich S, Cadlwell D, et al. A round robin programm on interfacial test methods. Compos Sci Technol 1993:205–14.

[185] Graupner N, Rößler J, Ziegmann G, Müssig J. Fibre/matrix adhesion of cellulose fibres in PLA, PP and MAPP: A critical review of pull-out test, microbond test and single fibre fragmentation test results. Compos Part A Appl Sci Manuf 2014;63:133–48. doi:10.1016/j.compositesa.2014.04.011.

[186] Baley C, Davies P, Grohens Y, Dolto G. Application of Interlaminar Tests to Marine Composites. A Literature Review. Appl Compos Mater 2004;11. doi:10.1023/B:ACMA.0000012902.93986.bf.

[187] Le Duigou A, Bourmaud A, Gourier C, Baley C. Multi-scale shear properties of flax fibre reinforced polyamide 11 biocomposites. Compos Part A Appl Sci Manuf 2016;85:123–9. doi:10.1016/j.compositesa.2016.03.014.

[188] Marrot L, Bourmaud A, Bono P, Baley C. Multi-scale study of the adhesion between flax fibers and biobased thermoset matrices. Mater Des 2014;62:47–56. doi:10.1016/j.matdes.2014.04.087.

[189] Le Duigou A, Kervoelen A, Le Grand A, Nardin M, Baley C. Interfacial properties of flax fibre–epoxy resin systems: Existence of a complex interphase. Compos Sci Technol 2014;100:152–7. doi:10.1016/j.compscitech.2014.06.009.

[190] Le Duigou A, Davies P, Baley C. Interfacial bonding of Flax fibre/Poly(l-lactide) bio-composites. Compos Sci Technol 2010;70:231–9. doi:10.1016/j.compscitech.2009.10.009.

[191] Manchado MAL, Arroyo M, Biagiotti J, Kenny JM. Enhancement of mechanical properties and interfacial adhesion of PP/EPDM/flax fiber composites using maleic anhydride as a compatibilizer. J Appl Polym Sci 2003;90:2170–8. doi:10.1002/app.12866.

[192] Garkhail S, Wieland B, George J, Soykeabkaew N, Peijs T. Transcrystallisation in PP/flax composites and its effect on interfacial and mechanical properties. J Mater Sci 2009;44:510–9. doi:10.1007/s10853-008-3089-9.

[193] Baley C, Grohens Y, Busnel F, Davies P. Application of Interlaminar Tests to Marine Composites. Relation between Glass Fibre/Polymer Interfaces and Interlaminar Properties of Marine Composites. Appl Compos

Mater 2004;11. doi:10.1023/B:ACMA.0000012884.02847.65.

[194] Le Duigou A, Bourmaud A, Balnois E, Davies P, Baley C. Improving the interfacial properties between flax fibres and PLLA by a water fibre treatment and drying cycle. Ind Crops Prod 2012;39:31–9. doi:10.1016/j.indcrop.2012.02.001.

[195] Baley C, Le Duigou A, Bourmaud A, Davies P, Nardin M, Morvan C, et al. Reinforcement of Polymers by Flax Fibers: Role of Interfaces. Bio-Based Compos. High-Performance Mater., CRC Press; 2014, p. 87–112. doi:doi:10.1201/b17601-7.

[196] Gindl W, Gupta HS. Cell-wall hardness and Young's modulus of melamine-modified spruce wood by nano-indentation. Compos Part A Appl Sci Manuf 2002;33:1141–5. doi:10.1016/S1359-835X(02)00080-5.

[197] Bos H, Molenveld K, Teunissen W, Van Wingerde A, Van Delft D. Compressive behaviour of unidirectional flax fibre reinforced composites. J Mater Sci 2004;39:2159–68.

[198] Alix S, Goimard J, Morvan C, Baley C. Influence of pectin structure on the mechanical properties of flax fibres: A comparison between linseed-winter variety (Oliver) and a fibre-spring variety of flax (Hermes). 2009. doi:10.3920/978-90-8686-677-9.

[199] Charlet K, Baley C, Morvan C, Jernot JP, Gomina M, Bréard J. Characteristics of Hermès flax fibres as a function of their location in the stem and properties of the derived unidirectional composites. Compos Part A Appl Sci Manuf 2007;38:1912–21. doi:10.1016/j.compositesa.2007.03.006.

[200] Pucci MF, Liotier P-JJ, Drapier S. Capillary effects on flax fibers - Modification and characterization of the wetting dynamics. Compos Part A Appl Sci Manuf 2015;77:257–65. doi:10.1016/j.compositesa.2015.03.010.

[201] Pucci MF, Seghini MC, Liotier P-J, Sarasini F, Tirilló J, Drapier S. Surface characterisation and wetting properties of single basalt fibres. Compos Part B Eng 2017;109:72–81. doi:https://doi.org/10.1016/j.compositesb.2016.09.065.

[202] Bourgois J, Guyonnet R. Characterization and analysis of torrefied wood. Wood Sci Technol 1988;22:143–55. doi:10.1007/BF00355850.

[203] Dirol D, Guyonnet R. The improvement of wood durability by ratification process. Doc. 40015, Int. Res. Gr. wood Preserv., IRG; 1993, p. 1–11.

[204] Pucci MF, Liotier P-JJ, Drapier S. Capillary wicking in flax fabrics - Effects of swelling in water. Colloids Surfaces A Physicochem Eng Asp 2016;498:176–84. doi:10.1016/j.colsurfa.2016.03.050.

[205] Pucci MF, Liotier P-J, Seveno D, Fuentes C, Vuure A Van, Drapier S. Wetting and swelling property modifications of elementary flax fibres and their effects on the Liquid Composite Molding process. Compos Part A Appl Sci Manuf 2017;97:31–40. doi:https://doi.org/10.1016/j.compositesa.2017.02.028.

[206] Ross K, Mazza G. Characteristics of Lignin from Flax Shives as Affected by Extraction Conditions. Int J Mol Sci 2010;11:4035–50. doi:10.3390/ijms11104035.

[207] Pucci MF, Liotier P-J, Drapier S. Capillary wicking in a fibrous reinforcement – Orthotropic issues to determine the capillary pressure components. Compos Part A Appl Sci Manuf 2015;77:133–41. doi:https://doi.org/10.1016/j.compositesa.2015.05.031.

[208] Bozaci E, Sever K, Sarikanat M, Seki Y, Demir A, Ozdogan E, et al. Effects of the atmospheric plasma treatments on surface and mechanical properties of flax fiber and adhesion between fiber–matrix for composite materials. Compos Part B Eng 2013;45:565–72. doi:https://doi.org/10.1016/j.compositesb.2012.09.042.

[209] Ventura H, Claramunt J, Navarro A, Rodriguez-Perez MA, Ardanuy M. Effects of Wet/Dry-Cycling and Plasma Treatments on the Properties of Flax Nonwovens Intended for Composite Reinforcing. Materials (Basel) 2016;9:1–18.

[210] Bourmaud A, Le Duigou A, Gourier C, Baley C. Influence of processing temperature on mechanical performance of unidirectional polyamide 11-flax fibre composites. Ind Crops Prod 2016;84:151–65.

doi:10.1016/j.indcrop.2016.02.007.

[211] Paris O, Zollfrank C, Zickler GA. Decomposition and carbonisation of wood biopolymers—a microstructural study of softwood pyrolysis. Carbon N Y 2005;43:53–66. doi:10.1016/j.carbon.2004.08.034.

[212] Zollfrank C, Fromm J. Ultrastructural development of the softwood cell wall during pyrolysis. Holzforschung 2009;63:248–53. doi:10.1515/HF.2009.031.

[213] Li Y, Yin L, Huang C, Meng Y, Fu F, Wang S, et al. Quasi-static and dynamic nanoindentation to determine the influence of thermal treatment on the mechanical properties of bamboo cell walls. Holzforschung 2015;69:909–14. doi:10.1515/hf-2014-0112.

[214] Zickler G., Schoberl T, Paris O. Mechanical properties of pyrolysed wood: a nanoindentation study. Philos Mag 2006;86:1373–86.

[215] Stanzl-Tschegg S, Beikircher W, Loidl D. Comparison of mechanical properties of thermally modified wood at growth ring and cell wall level by means of instrumented indentation tests. Holzforschung 2009;63:443–8. doi:10.1515/HF.2009.085.

[216] Yin Y, Berglund L, Salmén L. Effect of Steam Treatment on the Properties of Wood Cell Walls. Biomacromolecules 2011;12:194–202. doi:10.1021/bm101144m.

[217] Soccalingame L, Bourmaud A, Perrin D, Bénézet J-C, Bergeret A. Reprocessing of wood flour reinforced polypropylene composites: Impact of particle size and coupling agent on composite and particle properties. Polym Degrad Stab 2015;113:72–85. doi:10.1016/j.polymdegradstab.2015.01.020.

[218] Bourmaud A, Åkesson D, Beaugrand J, Le Duigou A, Skrifvars M, Baley C. Recycling of L-Poly-(lactide)-Poly-(butylene-succinate)-flax biocomposite. Polym Degrad Stab 2016;128:77–88. doi:10.1016/j.polymdegradstab.2016.03.018.

[219] Baley C, Le Duigou A, Bourmaud A, Davies P. Influence of drying on the mechanical behaviour of flax fibres and their unidirectional composites. Compos Part A Appl Sci Manuf 2012;43:1226–33. doi:10.1016/j.compositesa.2012.03.005.

[220] Gourier C, Le Duigou A, Bourmaud A, Baley C, Duigou A Le, Bourmaud A, et al. Mechanical analysis of elementary flax fibre tensile properties after different thermal cycles. Compos Part A Appl Sci Manuf 2014;64:159–66. doi:10.1016/j.compositesa.2014.05.006.

[221] Doumbia ASAS, Castro M, Jouannet D, Kervoëlen A, Falher T, Cauret L, et al. Flax/polypropylene composites for lightened structures: Multiscale analysis of process and fibre parameters 2015;87:331–41. doi:10.1016/j.matdes.2015.07.139.

[222] Lefeuvre A, Duigou A Le, Bourmaud A, Kervoelen A, Morvan C, Baley C. Analysis of the role of the main constitutive polysaccharides in the flax fibre mechanical behaviour. Ind Crops Prod 2015;76:1039–48. doi:10.1016/j.indcrop.2015.07.062.

[223] Li M, Tucker C. Modeling and simulation of two-dimensional consolidation for thermoset matrix composites. Compos Part A Appl Sci Manuf 2002;33:877–92. doi:10.1016/S1359-835X(02)00017-9.

[224] Michaud V. A Review of Non-saturated Resin Flow in Liquid Composite Moulding processes. Transp Porous Media 2016. doi:10.1007/s11242-016-0629-7.

[225] Svanberg MJ, Holmberg JA. Predictions of Manufacturing Induced Shape Distortions . Lulea University of Technology, Sweden , 2002.

[226] Masoodi R, Pillai KM. Modeling the processing of natural fiber composites made using liquid composites molding. Handb Bioplastics Biocomposites Eng Appl Ed by S Pilla, Scrivener-Wiley 2011.

[227] Nguyen VH, Deléglise-Lagardère M, Park CH. Modeling of resin flow in natural fiber reinforcement for liquid composite molding processes. Compos Sci Technol 2015;113:38–45.

[228] Masoodi R, Pillai KM. Darcy’s law-based model for wicking in paper-like swelling porous media. AIChE J

2010;56:2257–67.

[229] Gibson PW, Charmchi M. Modeling convection/diffusion processes in porous textiles with inclusion of humidity-dependent air permeability. Int Commun Heat Mass Transf 1997;24:709–24. doi:10.1016/S0735-1933(97)00056-0.

[230] Wisnom M, Gigliotti M, Ersoy N, Campbell M, Potter K. Mechanisms generating residual stresses and distortion during manufacture of polymer–matrix composite structures. Compos Part A Appl Sci Manuf 2006;37:522–9. doi:10.1016/j.compositesa.2005.05.019.

[231] Waris M, Liotier PJ, Drapier S. Effect of the mold on the residual strain field monitored with optical fibers sensors in resin transfer molding processes. J Compos Mater 2014;48:2589–601. doi:10.1177/0021998313501532.

[232] Pucci MF, Liotier P-J, Seveno D, Fuentes C, Vuure A Van. effect of thermal treatment on the interfacial properties of flax fibers. Conf Proceeding ICCM19, Copenhagen 2015:19–24.

[233] Pucci MF, Liotier PJ, Drapier S. Tensiometric method to reliably assess wetting properties of single fibers with resins: Validation on cellulosic reinforcements for composites. Colloids Surfaces A Physicochem Eng Asp 2017;512:26–33. doi:10.1016/j.colsurfa.2016.09.047.

[234] Blais M, Moulin N, Liotier P-J, Drapier S. Numerical simulation of resin infusion based processes on a new generation of structural reinforcements for aeronautics | Simulation num?rique du proc?d? par infusion de r?sine d'une nouvelle g?n?ration de renforts structuraux pour l'a?ronautique. Mater Tech 2016;104. doi:10.1051/mattech/2016027.

[235] Ouahbi T, Saouab A, Breard J, Ouagne P, Chatel S, Bréard JJ, et al. Modelling of hydro-mechanical coupling in infusion processes. Compos Part A Appl Sci Manuf 2007;38:1646–54. doi:10.1016/j.compositesa.2007.03.002.

[236] Darcy H. Les Fontaines Publiques de la Ville de Dijon. Victor Dalmont, Paris; 1856.

[237] Arbter R, Beraud JM, Binetruy C, Bizet L, Bréard J, Comas-Cardona S, et al. Experimental determination of the permeability of textiles: a benchmark exercise. Compos Part A Appl Sci Manuf 2011;42:1157–68.

[238] Lundstrom TS, Stenberg R, Bergström R, Partanen H, Birkeland PA. In-plane permeability measurements: a nordic round-robin study. Compos Part A Appl Sci Manuf 2000;31:29–43. doi:10.1016/S1359-835X(99)00058-5.

[239] Um M-K, Daniel IM, Childs BW. A gas flow method for determination of in-plane permeability of fiber preforms. Polym Compos 2001;22:47–56. doi:10.1002/pc.10515.

[240] Feser JP, Prasad AK, Advani SG. Experimental characterization of in-plane permeability of gas diffusion layers. J Power Sources 2006;162:1226–31. doi:10.1016/j.jpowsour.2006.07.058.

[241] Parnas RS, Salem AJ. A comparison of the unidirectional and radial in-plane flow of fluids through woven composite reinforcements. Polym Compos 1993;14:383–94. doi:10.1002/pc.750140504.

[242] Comas-Cardona S, Cosson B, Bickerton S, Binetruy C. An optically-based inverse method to measure in-plane permeability fields of fibrous reinforcements. Compos Part A Appl Sci Manuf 2014;57:41–8.

[243] Elbouazzaoui O, Drapier S, Henrat P. An experimental assessment of the saturated transverse permeability of Non-crimped New Concept (NC2) multiaxial fabrics. J Compos Mater 2005;39:1169–93. doi:10.1177/0021998305048746.

[244] Buntain MJ, Bickerton S. Compression flow permeability measurement: a continuous technique. Compos Part A Appl Sci Manuf 2003;34:445–57. doi:10.1016/S1359-835X(03)00090-3.

[245] Weitzenbock JR, Shenoi RA, Wilson PA. Measurement of three-dimensional permeability. Compos Part A Appl Sci Manuf 1998;29:159–69. doi:10.1016/S1359-835X(97)00049-3.

[246] Bréard J, Saouab A, Bouquet G. Mesure de la perméabilité spatiale d'un renfort tridimensionnel pour matériaux composites à matrice polymère. Eur Phys J AP 1998;1:269–78.

[247] Drapier S, Pagot A, Vautrin A, Henrat P. Influence of the stitching density on the transverse permeability of non-crimped new concept (NC2) multiaxial reinforcements: Measurements and predictions. Compos Sci Technol 2002;62:1979–91. doi:10.1016/S0266-3538(02)00127-6.

[248] Pomeroy R, Grove S, Summerscales J, Wang Y, Harper A. Measurement of permeability of continuous filament mat glass-fibre reinforcements by saturated radial airflow. Compos Part A Appl Sci Manuf 2007;38:1439–43. doi:10.1016/j.compositesa.2006.11.011.

[249] Nordlund M, Michaud V. Dynamic saturation curve measurement for resin flow in glass fibre reinforcement. Compos Part A Appl Sci Manuf 2012;43:333–43.

[250] Hou Y, Comas-Cardona S, Binetruy C, Drapier S. Gas transport in fibrous media: Application to in-plane permeability measurement using transient flow. J Compos Mater 2013;47:2237–47. doi:10.1177/0021998312455676.

[251] Drapier S, Monatte J, Elbouazzaoui O, Henrat P. Characterization of transient through-thickness permeabilities of Non Crimp New Concept (NC2) multiaxial fabrics. Compos Part A Appl Sci Manuf 2005;36:877–92. doi:10.1016/j.compositesa.2005.01.002.

[252] Slade J, Pillai KM, Advani SG. Investigation of unsaturated flow in woven, braided and stitched fiber mats during mold-filling in resin transfer molding. Polym Compos 2001;22:491–505. doi:10.1002/pc.10554.

[253] Puaux G, Silva L, Laure P, Vincent M, Coupez T. An immersed finite element method for permeability determination of a porous media. Int J Numer Meth Fluids 2010;00:1–24. doi:10.1002/fld.

[254] Silva L, Puaux G, Vincent M, Laure P. A Monolithic Finite Element Approach to Compute Permeabilityatc Microscopic Scales in LCM Processes. Int J Mater Form 2010;3:619–22.

[255] Chevalier L, Bruchon J, Moulin N, Liotier P-J, Drapier S. Accounting for local capillary e_ffects in two-phase _flows with relaxed surface tension formulation in enriched _finite elements. CR Mécanique 2018.

[256] Andriamananjara K, Chevalier L, Moulin N, Bruchon J, Liotier P-JJ, Drapier S. Numerical approach for modelling across scales infusion-based processing of aircraft primary structures. AIP Conf. Proc., vol. 1896, 2017. doi:10.1063/1.5007998.

[257] Gourichon B, Binétruy C, Krawczak P. A new numerical procedure to predict dynamic void content in liquid composite molding. Compos Part A Appl Sci Manuf 2006;37:1961–9. doi:10.1016/j.compositesa.2005.12.017.

[258] Spaid MAA, Phelan FR. Modeling void formation dynamics in fibrous porous media with the lattice Boltzmann method. Compos Part A Appl Sci Manuf 1998;29:749–55. doi:10.1016/S1359-835X(98)00031-1.

[259] Park CH, Lebel A, Saouab A, Bréard J, Lee W Il. Modeling and simulation of voids and saturation in liquid composite molding processes. Compos Part A Appl Sci Manuf 2011;42:658–68.

[260] Liu Y, Moulin N, Bruchon J, Liotier PJP-J, Drapier S. Towards void formation and permeability predictions in LCM processes: A computational bifluid-solid mechanics framework dealing with capillarity and wetting issues. vol. 344. 2016. doi:10.1016/j.crme.2016.02.004.

[261] De Parseval Y, Pillai KM, Advani SG. A simple model for the variation of permeability due to partial saturation in dual scale porous media. Transp Porous Media 1997;27:243–64.

[262] Tan H, Pillai KM. Multiscale modeling of unsaturated flow in dual-scale fiber preforms of liquid composite molding I: Isothermal flows. Compos Part A Appl Sci Manuf 2012;43:1–13.

[263] Pucci MF, Liotier P-J, Drapier S. Capillary wicking in a fibrous reinforcement–Orthotropic issues to determine the capillary pressure components. Compos Part A Appl Sci Manuf 2015;77:133–41.

[264] Lawrence JM, Neacsu V, Advani SG. Modeling the impact of capillary pressure and air entrapment on fiber tow saturation during resin infusion in LCM. Compos Part A Appl Sci Manuf 2009;40:1053–64.

[265] Parnas RS, Salem AJ, Sadiq TAK, Wang HP, Advani SG. The interaction between micro- and macro-scopic flow in {RTM} preforms. Compos Struct 1994;27:93–107.

[266] Lopez E, Leygue A, Abisset-Chavanne E, Comas-Cardona S, Aufrere C, Binetruy C, et al. Flow modeling of linear and nonlinear fluids in two scale fibrous fabrics: Advanced simulations. Int J Mater Form 2017;10:317–28. doi:10.1007/s12289-015-1280-5.

[267] Lagardère M, Park CH, Panier S, others. Permeability of natural fiber reinforcement for liquid composite molding processes. J Mater Sci 2014;49:6449–58.

[268] Washburn EW. The dynamics of capillary flow. Phys Rev 1921;17:273.

[269] Wehner JA, Miller B, Rebenfeld L. Moisture Induced Changes in Fabric Structure as Evidenced by Air Permeability Measurements. Text Res J 1987;57:247–56. doi:10.1177/004051758705700501.

[270] Francucci G, Rodr\'\iguez ES, Vázquez A. Study of saturated and unsaturated permeability in natural fiber fabrics. Compos Part A Appl Sci Manuf 2010;41:16–21.

[271] Potluri P, Parlak I, Ramgulam R, Sagar T V. Analysis of tow deformations in textile preforms subjected to forming forces. Compos Sci Technol 2006;66:297–305. doi:10.1016/j.compscitech.2005.04.039.

[272] Bouquerel L, Moulin N, Drapier S, Boisse P, Beraud J-M. Modelling and simulating the forming of new dry automated lay-up reinforcements for primary structures. AIP Conf. Proc., vol. 1896, 2017. doi:10.1063/1.5007995.

[273] Liotier P-J, Govignon Q, Swery E, Drapier S, Bickerton S. Permeability of sheared woven flax fibres reinforcements; Definition of parameters to model complex shape composites part processing by LCM. 16th Eur. Conf. Compos. Mater. ECCM 2014, 2014.

[274] Fuentes CA, Ting KW, Dupont-Gillain C, Steensma M, Talma AG, Zuijderduin R, et al. Effect of humidity during manufacturing on the interfacial strength of non-pre-dried flax fibre/unsaturated polyester composites. Compos Part A Appl Sci Manuf 2016;84:209–15. doi:https://doi.org/10.1016/j.compositesa.2016.01.023.

[275] Campana C, Leger R, Sonnier R, Ferry L, Ienny P. Effect of post curing temperature on mechanical properties of a flax fiber reinforced epoxy composite. Compos Part A Appl Sci Manuf 2018;107:171–9. doi:https://doi.org/10.1016/j.compositesa.2017.12.029.

Table 1: Influence of the type of test on the measured apparent interfacial shear strength [185].

Materials	Pull-out test Apparent Interfacial Shear Stress IFSS (MPa). Mean value	Fragmentation Apparent Interfacial Shear Stress IFSS (MPa). Mean value	Ratio Pull-out/ fragmentation
Flax/PP	17.9 ± 10.5	9.8 ± 6.8	1.8
Flax/MAPP	24.3 ± 11.1	36 ± 15.8	0.675

Table 2: Apparent interfacial shear strengths (IFSS) measured by the microdroplet test. All tests performed in the same laboratory with the same test fixture.

Fibre	Polymer	Thermoset	Thermoplastic	IFSS (MPa)	References
Glass	Polyester	X		15.7 ± 2.9	[186]
Glass	epoxy	X		29.3 ± 2.4	[186]
Glass	polyester	X		16.1 ± 0.5	[181]
Flax	PA11		X	22.3 ± 3	[187]
Flax	PLA		X	15.3 ± 3.3	[39]
Flax	epoxy	X		16.1 ± 0.8	[39]
Flax	polyester	X		14.2 ±0.4	[181]
Flax	epoxy	X		22.3 ± 2.1	[36]
Glass	epoxy	X		37.2 ± 4.6	[36]
Flax	polyester	X		17.5 ± 7.3	[188]
Flax	epoxy	X		20.4 ± 4.9	[188]

Table 3. Composite manufacturing processes.

AM[1] : Additive Manufacturing. AFP[2] : Automated Fiber Placement. ATL[3] : Automated Tape Laying. LRI[4] : Liquid Resin Infusion. RFI[5] : Resin Film Infusion. RTM[6] : Resin Transfer Molding. CRTM[7] : Compression Resin Transfer Molding

<table>
<tr><th rowspan="2">Shape composite part</th><th rowspan="2">Family of technologies</th><th rowspan="2">Fiber ratio L/d</th><th colspan="3">Multi-Physics and Multi-Scale Couplings</th></tr>
<tr><th>Thermo-Chemo</th><th>Hydro</th><th>Mechanical</th></tr>
<tr><td>Profile</td><td>Pultrusion</td><td rowspan="5">Long fiber > 1000</td><td rowspan="8">Thermo-kinetic cycle

Thermoset / Thermoplastic</td><td>Bath
UD Tape
Prepreg</td><td>Pultrusion die
Pulling force</td></tr>
<tr><td rowspan="2">Revolution</td><td rowspan="2">Filament Winding</td><td rowspan="2">Film
powder
Gates, vents, and runners</td><td>Tension control</td></tr>
<tr><td rowspan="2">3D
(without press
1 mold)</td><td rowspan="2">- AM[1] (without mold)
- AFP[2], ATL[3]
- Autoclave
- LRI[4], RFI[5]</td><td>Compaction roller</td></tr>
<tr><td rowspan="2">Gates, vents, and runners</td><td>Flexible membrane

Semirigid countermold</td></tr>
<tr><td>3D
(without press
2 molds)</td><td>- RTM[6]</td><td rowspan="3">Rigid tool</td></tr>
<tr><td rowspan="2">3D
(with press
2 molds)</td><td>- CRTM[7]
- Compression Molding</td><td></td></tr>
<tr><td>- Injection molding
- Extrusion</td><td>Short fiber or Particles < 1000</td><td>Fiber
Film
Powder
Compound</td></tr>
</table>

Figure 1. Microscope image of section perpendicular to fibres in unidirectional composite, showing individual flax fibres and bundles [53]

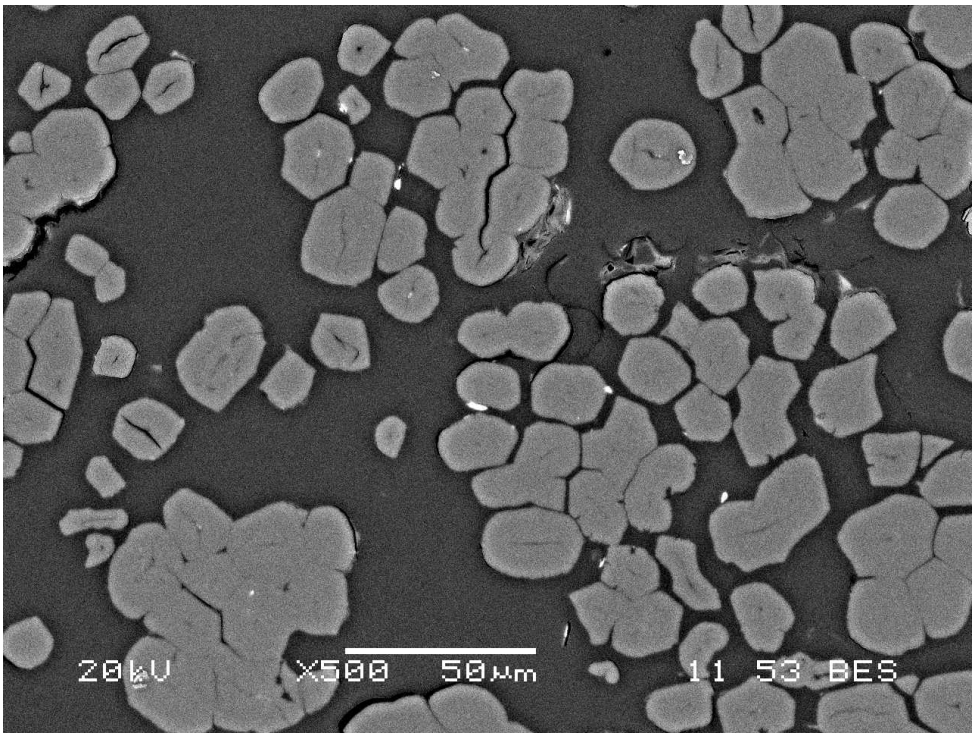
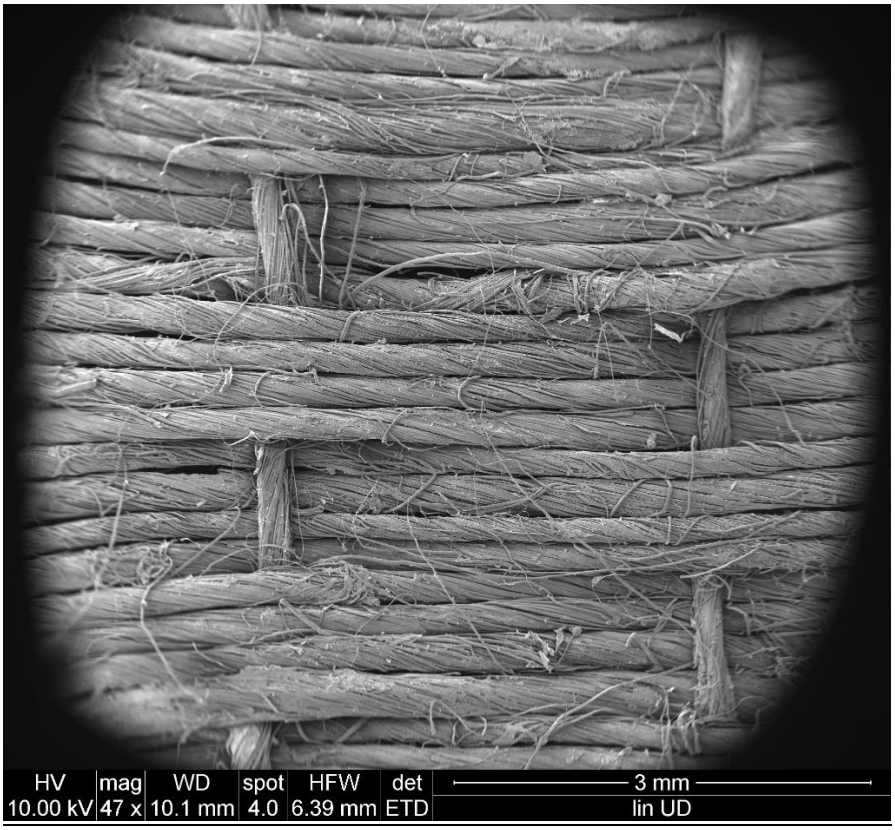


Figure 2 : Quasi-unidirectional flax preform made up of twisted fibre assembles.



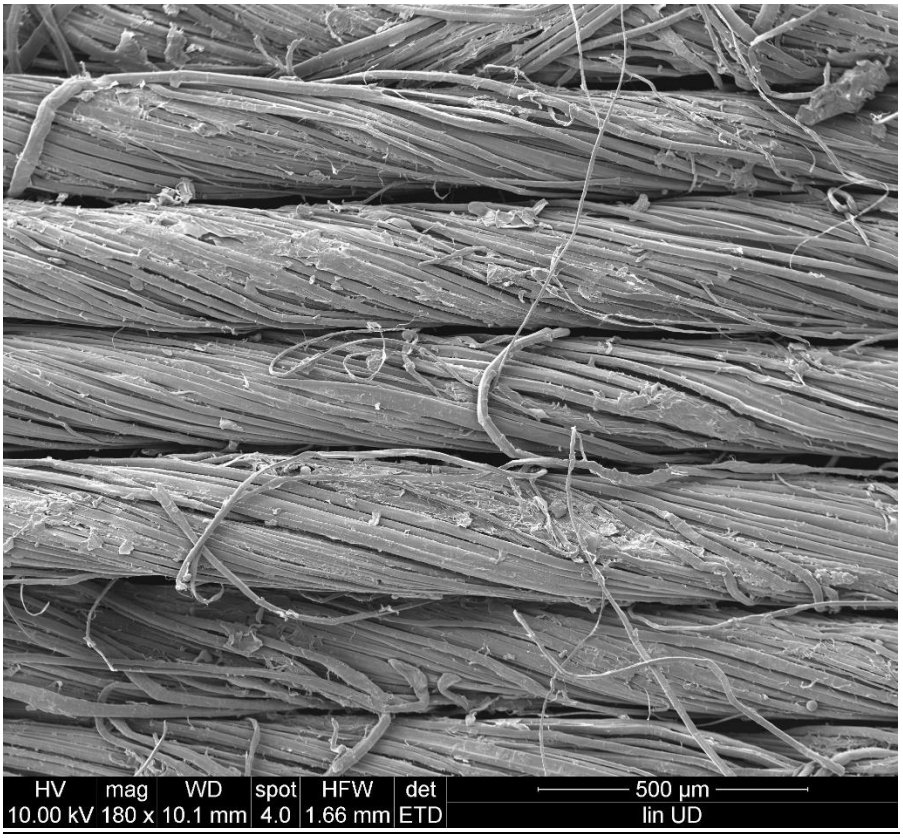


Figure 3. Upper: Example of lay-up of unidirectional flax plies impregnated by a thermoplastic matrix (PP-AMPP) manufactured by film stacking, showing interlaminar voids and a poor spatial fibre distribution through the ply thickness. Lower: Example of a lay-up of unidirectional flax impregnated by thermoplastic matrix (PP) manufactured by compression moulding, showing good material quality [41].

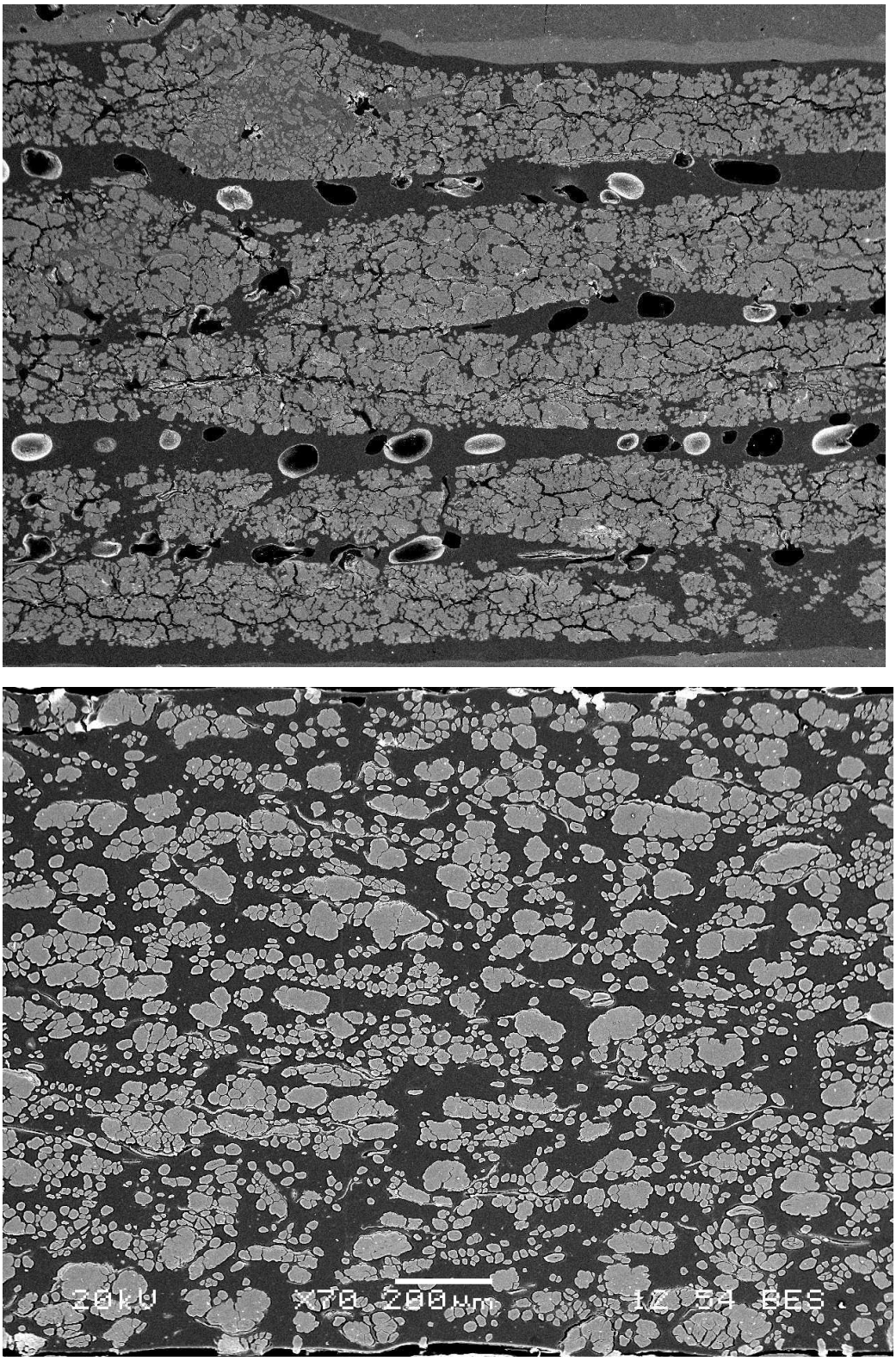


Figure 4. Photograph of flax fibres samples with different degrees of retting. From unretted sample (R1) on the left to retted sample on the right (R6) [67].

Figure 5. Defects during the weaving process. Left: Broken free glass fibres [91]. Right: broken carbon monofilament [92]

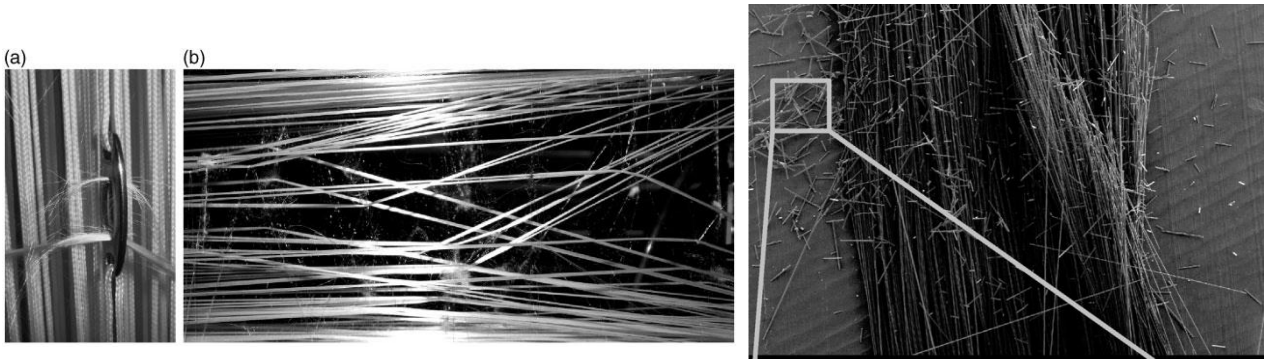


Figure 6. Upper: Samples of flax nonwoven fabrics (areal density of 330 g/m^2) [109].

Lower: Cross-section of Flax/PP non-woven fabric after needle-punching [110].

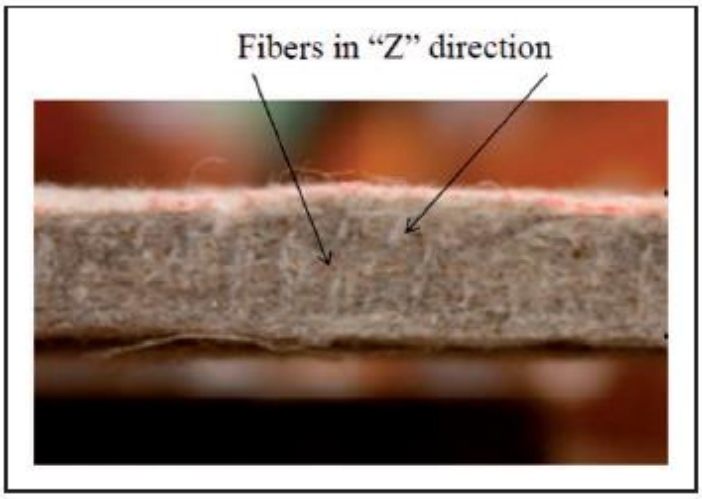


Figure 7. Flax yarn assembled by adhesive bonding

Figure 8. Fibre spinning (left) [147]. Right: Typical effect of twist on yarn strength [128].

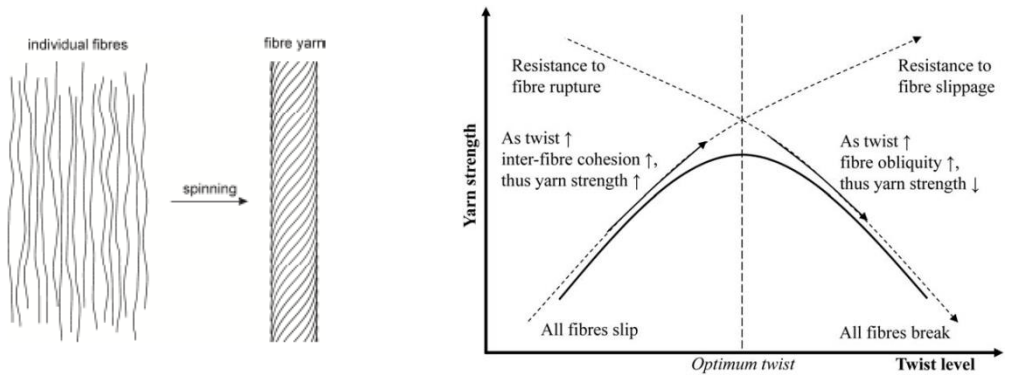


Figure 9. Influence of twist level on Tenacity (Left) and deformation at break (Right) of flax yarns.

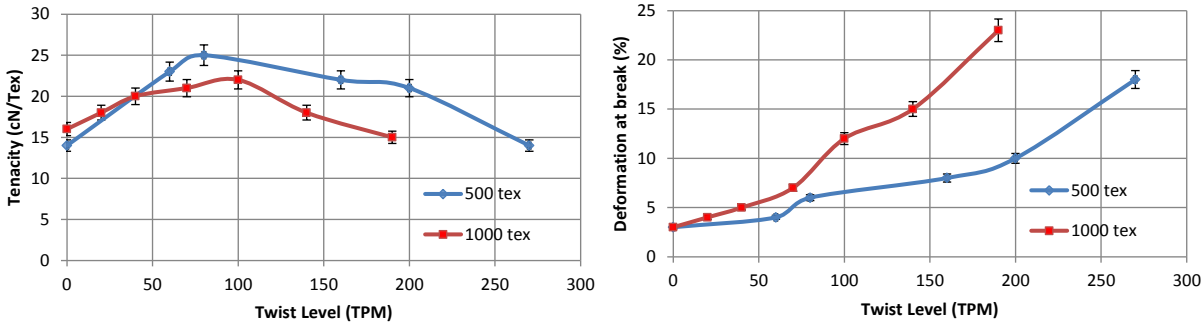
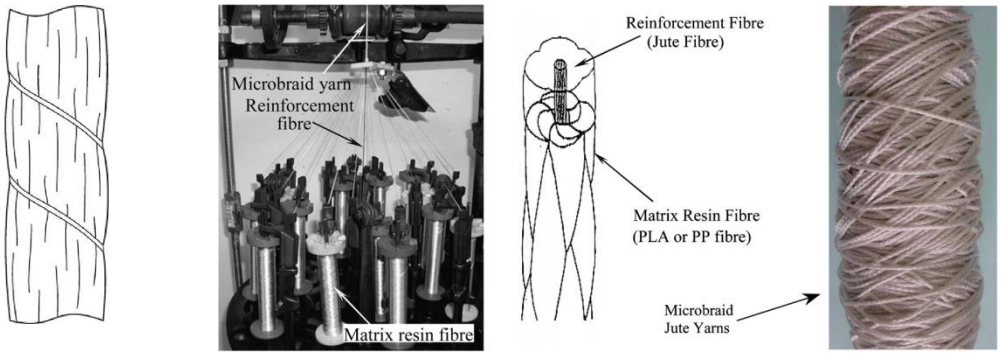


Figure 10. Left: Warping staple natural fibres with a thread [111]. Right: Micro-braiding technology [155]. Below: DREF-3 spinning system [156][157]



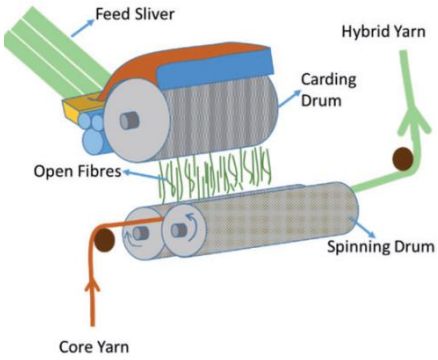


Figure 11. Left: Braiding Loom. Right: Biaxial braids from Flax/PA12 yarns [148]

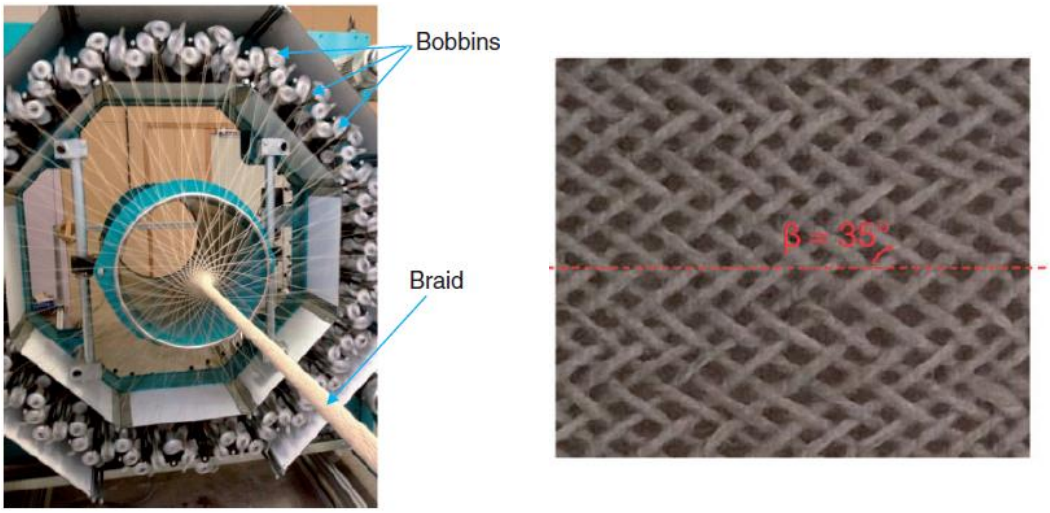
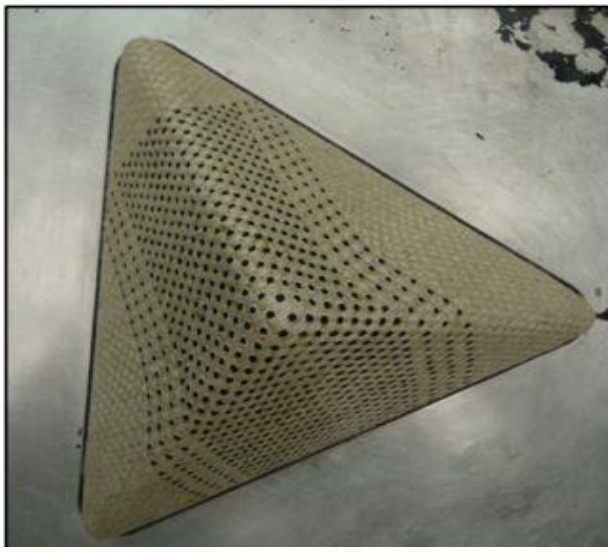
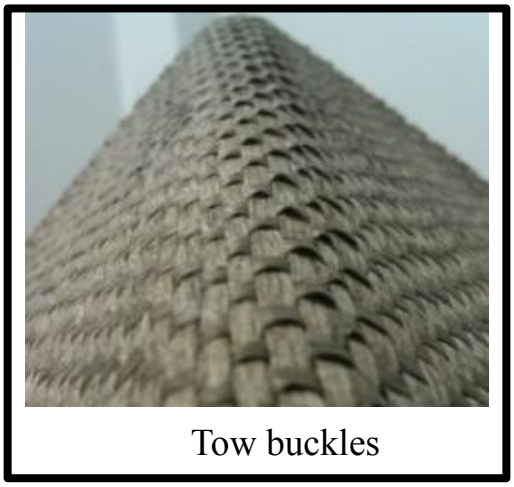


Figure 12. Manufacture of 3D-warp interlock from flax rovings [148]

Figure 13: Forming of complex shapes (a); Appearance of tow buckling (b)



(a)



(b)

Figure 14: Elementary Flax fibre after retting, showing remains of middle lamella on the surface [181].

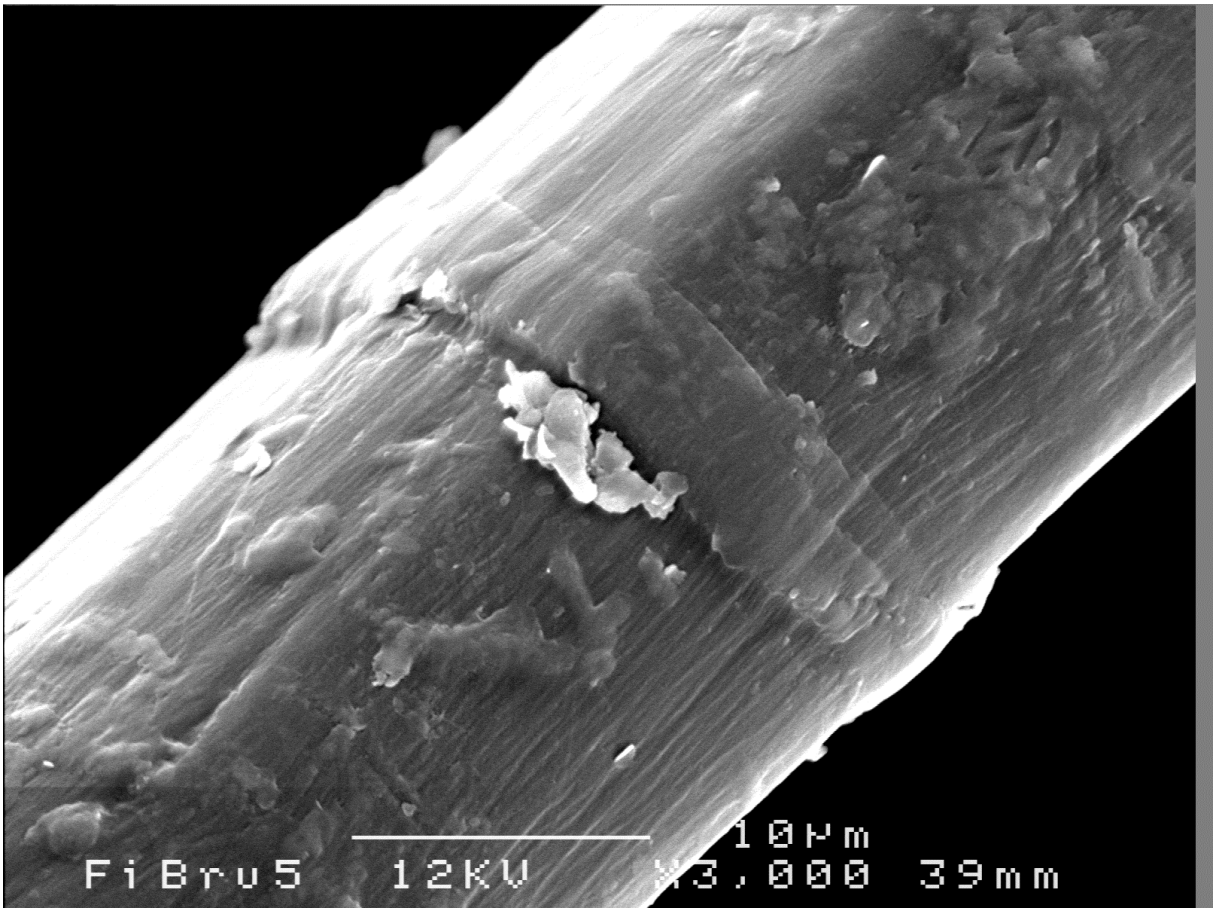


Figure 15 : Elementary flax fibre after surface cleaning by a chemical treatment.

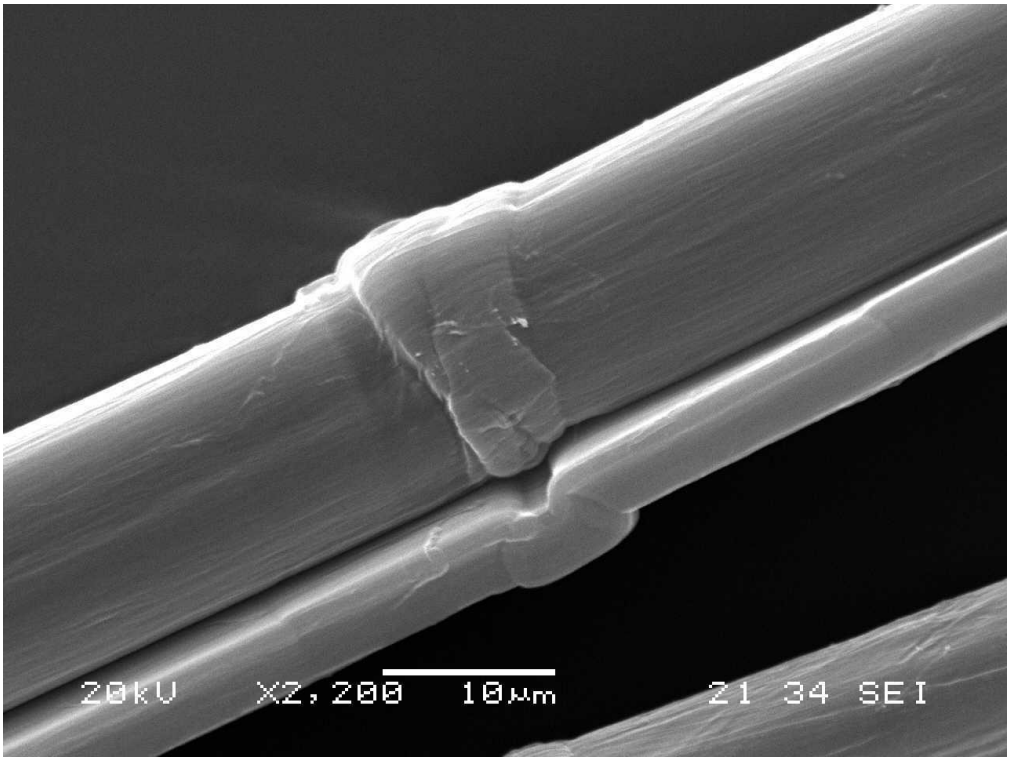


Figure 16. (Left) Schematic diagram of microdroplet test [190], (Right) Typical debonding behaviour [192]

A.

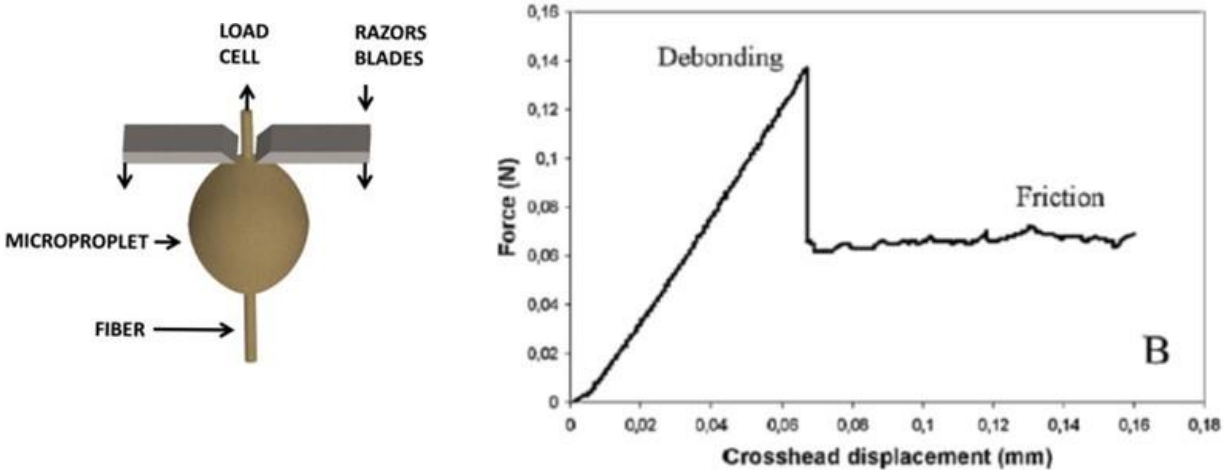
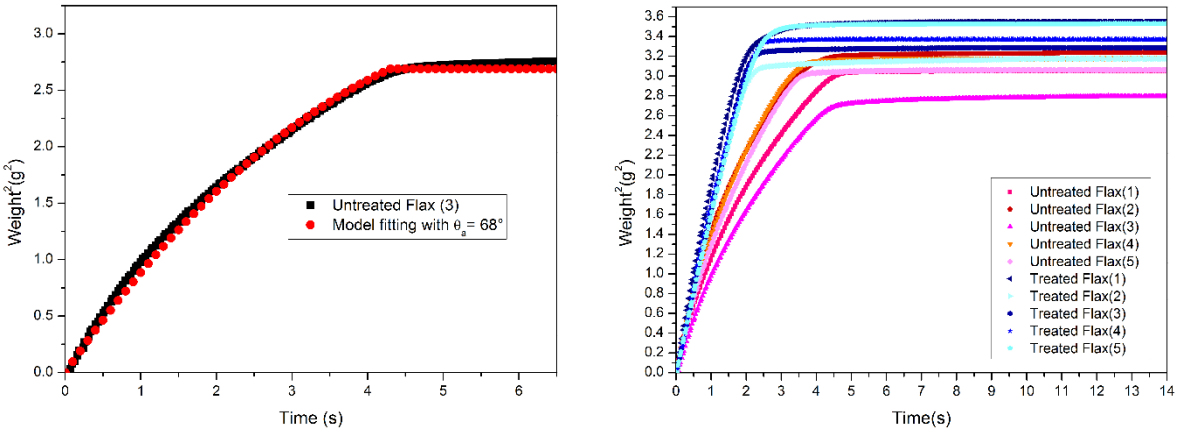


Figure 17: Squared mass intake over time in wicking tests for quasi-UD at 35% fibre volume fraction - fibre direction - for (a) untreated and treated flax preforms, and (b) untreated flax preform fitted with a non-linear Washburn's modified theory accounting for swelling with the corresponding advancing contact angle identified through this model; from [204].



(a) (b)