TOWARDS HIGH-PERFORMANCE BIOCOMPOSITES FOR TARGETED APPLICATIONS: HOW CAN WE BEST DEFINE THE DIVERSITY AND SPECIFICITIES OF REINFORCEMENT PLANT FIBRE CELL WALLS?

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Abstract

For the past 15 years, there has been tremendous and ever-increasing industrial and academic interest and technological material development concerning plant fibre reinforced composites. Plant fibres can be sourced from a multitude of natural agro-sources, with the preferred choice as a composite reinforcement material often being driven by abundance, geographical location, and historical use. While from a product designer's or engineer's point of view, all plant cell walls are 'similar', there is indeed substantial diversity in plant fibre cell walls. Indeed, a growing body of research demonstrates how cell wall mechanical behaviour is strongly linked to its

structure, biochemical composition and the plant growing conditions. At the same time, significant progress has been realised on the knowledge of plant fibre cell wall reinforcement mechanisms in biocomposites. Here, we provide a holistic overview of the main types of plant cell walls used as reinforcements for polymer composites. By synthesising a large body of bibliographic data, we present and discuss the useful diversity in cell walls, illustrated by original schematics for clear comparison. The link between their structures and main properties, in constant link with potential associated composite, is specifically discussed. Then, the different fibre extraction and cultivation modes are discussed and compared, especially through an environmental assessment. We also show how a scientist's point of view on cell wall structure and associated experimental approach and use of characterisation techniques lead to distinct results; following a critical review, we make recommendations on appropriate characterisation techniques for a specific fibre. A final discussion concludes this work by highlighting the pertinent parameters that accurately define a composite reinforcement cell wall. The review will serve as a useful handbook reference for researchers in the field of bio-based materials, and will provide important insights to designers and engineers for appropriate selection of plant fibre cell walls for specific composite applications.

Keywords: Plant cell wall; Natural fibre; Composite; Mechanical properties; Structure; Characterisation

1. Introduction

Mankind has utilised plant fibres for at least over 40,000 years [1]. Understanding when, how and why ancient civilizations have used these natural materials can inform us of their development story. Animal wool and flax were used to develop the world's first textiles, according to the concerned geographical area. The first trace of linen comes from dating a grain of pollen of this plant, trapped in sediments in Iran 34,000 years ago. Flax has truly accompanied the history of man and the birth of agriculture in the Neolithic period (about 10,000 years BC) in Mesopotamia and throughout the Fertile Crescent [2]. Water-

retted samples have been found in ancient lake dwellings in Switzerland and have been dated to about 8,000 years BC. This treatment with water facilitated the individualization of flax elementary fibres, arranged in bundles in the phloem of the stem, through removal of adjoining lamellae residues, making the fibres suitable for fine textile applications. It testifies to the advanced technology of these ancient civilizations that have developed water-retting, one of the oldest known biotechnology [3]. Other plant fibres, such as hemp, have a similar history. The oldest traces of this plant have been found in China and dated to about 8,000 BC. It accompanied the history of mankind for the quality of its fibres, but also for its seed-oils and medicinal properties [4,5].

Today, the continual and unsustainable rise in the global consumption of non-renewable resources, such as petroleum, as well as renewable resources, such as water, is an urgent matter of concern – at least to us climate alarmists [6,7]. Another problem under intense discussion is that of climate change due to human activities, mainly carbon dioxide emissions [8,9]. The growing needs of humankind, due largely to increasing rates of world population growth and adoption of modern life-styles, has meant a substantial increment in the consumption of synthetic materials. Not surprisingly, major importance is now attributed to the use of renewable materials in the manufacture of industrial components. Thus, environmental and economic concerns are stimulating research in the development of new materials for construction, consumer products, packaging and transportation industries [10–12]. Particularly attractive are materials derived from natural, renewable resources which prevent further stress on the environment, such as that caused by the depletion of already dwindling wood resources from forests. Examples of such raw material sources are annual-growth native crops, plants and fibres that are abundantly available in occidental or tropical regions [13–15]. These plants and fibres - such as flax, hemp, jute and sisal - have been used for thousands of years for many applications, including ropes, beds, and bags. If new uses of fast-growing native plants can be developed for high value applications, they could offer a tremendous potential for creating jobs in the rural sector.

Plants and their derivative products are also sources of inspiration for engineering designs, and there has been a strong interest for research on biomimetic in recent years [16,17]. Plant structures have outstanding mechanical performances, which are the result of a long evolutionary process of optimization, and the current socio-economic context of resource and energy conservation favours this approach. In plants, the role of fibres can be very diverse. In the stem (wood, flax, hemp), they generally act as supporting tissues for plant stability. They can also have a protective role and improve the impact resistance of fruit (coconut), enable sap conduction (wood) or allow the dissemination of seeds by wind (cotton). We can also find them within leaves (sisal for example). Thus, according to their location in the plant, function and morphology varies, and consequently so do their structural arrangement and mechanical properties [18].

The morphological and mechanical properties of the fibres from plants are key parameters for producing polymer composites. The mechanical properties are mainly influenced by the value of the ratio of cell wall thickness to fibre diameter, but also by the morphology and the structure of the fibres; we have to keep in mind that an elementary plant fibre is also a elementary cell, having all characteristics of this primary element. Plant fibres are described by endogenous parameters such as the fraction of cellulose and its crystallinity, the polysaccharide composition of the cell walls [19] and the MFA which represents the orientation of the cellulose fibrils relative to the axis of the fibre [20]. These parameters are influenced by the genetic determinism and pedoclimatic factors such as weather, culture line (inputs, seeding, crop rotation) or the nature of the soil [21,22]. Biotechnological methods used for the extraction of plant fibres also have significance in the final quality of the fibres. Retting conditions will directly affect the fibre morphology and mechanical properties and also dictate the adhesion mechanisms between plant cell walls and thermoplastic or thermoset matrices [23,24].

There is a tendency to refer to plant fibres generically, and consider even fibres from different origins to be 'similar', however, they can have very different properties which may suit different applications. This knowledge is of particular importance for the rational development of biocomposites. However, the determination of relevant mechanical and

structural parameters, given the complexity of the cell walls and small scales of observation, is not trivial, and the characterization of the structure and performance demands precautions. In addition, scientists working on this topic have diverging views, with their background greatly influencing their understanding and interpolations of studied phenomena. By looking at the same live objects, biologists, physicists or engineers do not 'see' the same thing and also do not (usually) have the same panel of investigative techniques. In the case of plants, biologists are mainly interested in the regulation of metabolism and flows in the parietal cells and consecutive impacts on molecular composition. Physicists, on the other hand, wonder how forces and pressures are distributed and resisted in the cells And stem structure. These two ways of looking at things are complementary but can lead to different approaches and conclusions. in this review we will focus on linking the properties, performance and main characteristics of plant fibres to future composite applications. The choice of the reinforcing fibres must be made by continuously taking into account the final application and the composite materials, which requires state-of-the-art, if not near-complete, knowledge of the fibres, but also of the processes for making the composites and the relationship between the fibre characteristics and the performance of the plant fibres composites. In this paper, plant fibres will be described and considered regarding their use in both short and long fibres composites, i.e. extruded, injected and also compressed or infused materials; indeed, the quality or the morphology of plant fibres can influence their final use.

Through this review, we first propose a classification of the different families of fibres belonging to different plants. We will focus on the differences in fibre properties, related to cell structure, arising from the location within the plant. We will also examine the different fibre extraction techniques and their multi-faceted impacts fibre quality and properties, as well as on the environment and ecosystem. The second part of this review will discuss the divergent views on plant fibre structures in literature, principally arising from the variety of investigative techniques and associated interpretations. The impact of the type of fibres, their properties and major biotechnology implemented on the final quality of the produced biocomposites will also be reviewed.

2. Plant cell walls: a significant variety of morphologies and properties

2.1. Overview of plant fibre diversity

2.1.1. Classification according to origin

Nature offers a large diversity of plant fibres which are generally classified according to their location within plants (Figure1).

Figure 1

As materials and reinforcements in composites, plant fibres are used in a number of applications and are of high technical and commercial importance [26–28].

Plant fibres display different classes of fibres such as bast, straw, seed, grass, leaf, and wood fibres. Due to their specific functions and location in plants, these fibres exhibit a large panel of structural properties, and consequently mechanical performances. For example, coconuts provide coir fibres which play the role of environmental and mechanical protection around the fruit, while hemp fibres are the supporting tissues of the stem, and cotton fibres are wrapped around the seeds in order to facilitate their spreading by the wind. The relationship between the role, the structure and the fibres properties will be discussed later.

2.1.2. State of the uses; techno-economic data

It is not easy to obtain reliable cost data for plant fibres. Indeed, prices depend on the availability of the resource, raw material sales volumes, as well as the quality of the fibres (vis. length, visual properties, mechanical properties). Moreover, costs for fibre extraction, chemical treatment and transportation may vary considerably.

Classification of plant fibres presented in Figure 1 can also take the form of that shown in Figure 2 [29]. It supplements the usual classification by origin in the plant with whether the plants are

grown specifically for their fibres (so called primary fibres [29]) or if the fibres are a by-product of some other primary use of the plant (so called secondary fibres [29]).

Figure 2

The classification into primary and secondary fibres is relevant as prices depend on the use of the plant. For example, in France the predominant market for fibres from annual plants (excluding textiles) is those of particleboards, accounting for about 85% of processed volume, far ahead of the concrete (10%), insulation (3%) and composites (2%) markets [30]. Figure 3 shows a comparison between the cost of vegetal and glass fibres.

Figure 3

As we can see from Figure 3, plant fibres cover a wide range of prices. Some, like alfa and bamboo, are available at very low prices and are very competitive compared to glass fibres. Others display significantly higher costs; this is generally the case of long fibres such as flax or hemp, and we shall return to this notion of length a little further. One can also note that coir fibres, considered as secondary fibres, also display a low cost. Even within the same species of plant, prices can show large differences; this is for example the case for cotton, hemp and sisal. These differences are justified by differences in fibre quality that are linked to their finesse, their surface state or to their mechanical strength. These price differences can also be caused by changes in supply and demand, as is the case for commodities in general. Due to the density and mechanical performance differences between plant and synthetic fibres, some authors have considered it more relevant to compare their cost per unit functionality (such as specific mechanical properties). However, as we argue later properties such as density and strength can sometimes be problematic to compare due to the very different fibre structures and morphology between species.

Figure 4 shows the country repartition of abaca, coir, flax, hemp, jute, kapok, kenaf and sisal fibre production for 2013. Global fibre production is shown in the map below with data for each area of production and kind of fibre. Due to their high production quantities, cotton and wood fibres are presented in separate graphs (Figure 6). Firstly, one can notice that natural fibres are produced in many countries but the main quantity comes from Asia, especially due to the high quantity of jute fibre produced in India and Bangladesh. In tropical countries, such as Brazil (sisal), Ecuador and Philippines (abaca), India (coir and jute), Pakistan and Bangladesh (jute and coir), China (ramie and hemp), there exist a large variety of plant fibres with different mechanical, physical and chemical characteristics. The list of fibres with composite reinforcement potential which are grown in those countries mainly includes sisal, jute, kapok, abaca, abaca, coir and ramie.

Figure 4

Thus, plant fibres are produced in some of the lowest-income areas of the world. The countries that produce the fibre include several that are classified as being Least Developed Countries (LDCs), where the average annual gross income per capita is below US$ 750 [38]. This is for example the case for sisal cultivation in Tanzania, where the rural populations of these areas are therefore particularly dependent on sisal, which represents one of the few sources of dependable cash income. In periods of pronounced drought, sisal offers the only hope of maintaining sufficient purchasing power and consequently provide some assurance of food security. This is the case not only in producing countries of the LDC category, but also in the world's largest sisal producer, Brazil. In this country, production of sisal is concentrated in the very low-income, arid areas of the north-eastern region, where alternatives for rural income generation are limited or non-existent. In these arid areas, sisal cultivation provides one of the

few viable agricultural production alternatives to generate income and supplement on-farm food production. Outside these economic considerations, plant fibre cultivation contributes also to environmental progress; one can notice the replacement of asbestos in cement by sisal which is a particular aspect of the market for construction materials that has gained ground as the prohibition of asbestos has gained momentum, particularly in some highly populous countries such as Brazil. Due to their environmental advantages, plant fibres have also penetrated the transportation sector, especially the automotive industry, whatever the kind of fibre. In order to reach the maximum market potential and to plant factories all over the world, the major automobile manufacturers are looking for reliable local fibre availability. While specific tests have not yet been carried out exhaustively for certain fibres due to the difficulty in obtaining suitable production data, the results obtained with fibres produced in relatively higher-income countries such as flax and hemp indicate that the substitution of glass fibre leads to a significant reduction in non-renewable energy requirements during the production phase [40]. However, contrary to the general but widely stated notion, the environmental benefit in using plant fibres can be moderate. This will be specifically discussed in Section 2.5.3.

Figure 5 shows the main areas and quantities of production for cotton [38] and wood fibres. Global production of wood fibre in 2014 amounted to 401 million tons [41]. The main producers were the USA, China, Japan, Brazil and Canada, and together, these countries produced 59% of the global total. The Asia-Pacific region is now the largest producer of wood fibre and Brazil, where fast-growing planted forests give the country a competitive advantage in the manufacturing of wood pulp will probably overtake Canada to become the fourth-biggest producer in the next few years.

Figure 5

Cotton production is mainly governed by China and India, followed to a lesser extent by USA, Pakistan and Thailand. In the past few years, we have seen an important increase in China's

cotton fibre stocks, leading to price increases. Nevertheless, consumption is currently decreasing in China due to the reduction of state support for its farmers. Thus, there is a slight evolution of the production towards low-yield countries in South-Asia and Sub-Saharan Africa.

In temperate climate countries such as Europe, flax and hemp are the most representative.

Figure 6

Flax and hemp occupy only a marginal place in world production of natural fibres (respectively 2.4% and 0.3% of world production) largely dominated by cotton and wood. If we focus specifically on flax (Figure 6), France is the largest producer with about 50% of production in 2014. Europe represents about two thirds of world production and flax is characterized by high yields of around 1.5 t / ha. China and Russia have relatively low production levels in view of the importance of cultivated areas; apparent yields being very low. A few anecdotal productions in terms of volume are present in Egypt and in the Baltics.

2.2. Plant fibres: a large range of reported properties

2.2.1. A large range of properties among the different plant cell walls

In literature, many authors have studied plant fibres and one can find a large amount of morphological, mechanical, structural and biochemical data concerning these fibres. For composite applications mechanical and morphological properties directly impact the quality of materials; composite mechanical performances are generally well-correlated with that of the reinforcement. Reinforcement aspect ratio (L/D) is also an important parameter for efficient stress transfer between fibre and matrix.

Table 1 amalgamates data available in literature concerning the morphology of the fibres. Length, diameter, the cellulose microfibril angle relative to the longitudinal axis of the fibre

(MFA) and density are tabulated for common plant fibre reinforcements used in biocomposites. Values listed here relate to elementary fibres.

Table 1

One can see that some morphological characteristics are highly variable from one plant to another. If the densities or the diameters of the elementary cells do not vary much, it is not the case for the MFA. This latter varies substantially between plant types and, as we will see later, can lead to significant differences in terms of mechanical behavior. Moreover, the value of this angle is not fixed for a given species and may fluctuate among plant varieties of the same species. This is particularly the case for wood cell walls where the angle may have a value of about 5 ° in the gelatinous (G) layer of the tension wood, between 10 and 20 ° for normal wood or from 30 to 45 ° in the case of compression wood [96,97]. The difficulties in MFA measurements, inducing uncertainties, will be detailed in the second part of this review. In terms of the morphology of the elementary fibres, we can also see significant variations regarding the length of the cells. These can be very short in the case of jute, bamboo, wood, kenaf or alfa but also much longer for plants such as ramie, flax or hemp. These differences in length can of course, as we shall see later in this document, impact the handling of fibres, as well as their extraction but also on experimental devices available for their characterisation.

The concept of length becomes preponderant in the case of the mechanical characterisation of fibres. It is also a major point for composite materials, directly influencing the aspect ratio of reinforcements; indeed, for composites the quality of stress transfer between fibre and matrix is strongly linked to the individualisation of fibres and interfacial area which are directly influenced by reinforcement length/diameter ratio. As discussed in the second part of this manuscript, tensile mechanical properties are largely influenced by the nature of the fibre elements (elementary fibres or bundles). Thus in literature, characterised objects are not always elementary fibres, numerous works on bundles have been presented, often without the nature

of the element (elementary fibre or bundle) being specified clearly. In Table 2, we have grouped results from tensile tests conducted on different species of plant fibres.

Table 2

When data was available, we have reported the results of elementary fibres as they are more representative of the 'smallest' element. In some cases, because of small fibre lengths, only test results on bundles exist. Thus, the values that we can find in the literature are sometimes be difficult to compare, not only for the reasons just mentioned above but also because of the number of selected tests. For example, the data presented in table 2 for alfa fibres concern 2 batches of fibre given the lack of studies in the literature; when in the case of flax, more than 60 lots are summarized in this table. This can generate more dispersion and disparity in the results. Moreover, as these experiments require an important know-how, the quality of the experimenter plays an important role on the results, as well as the machine used, the test conditions and the method of analysis.

If one focuses on the elementary fibres (Figure 7) we see a clearly marked hierarchy between the elementary fibres in terms of strength and stiffness. We note on this graph the presence of two populations of fibres, shown by the two dotted trend lines. Within the first group of fibres, corresponding to the lowest black dotted regression line, flax fibres, are clearly distinguishable by its superiority from other varieties; although alfa fibres and ramie compete with them, data are only available for those species on few batches which does not allow to draw clear conclusions about the reproducibility of their performance.

Figure 7

We can then note the weaker performance of hemp fibres (penalised by short secondary fibres) and even reduced for those of kenaf and kapok; we will see a little further that these latter fibres are penalised by their very specific morphology due to the thickness of their cell wall. The second group of fibres (red dotted regression line) is made of wood, bamboo and cotton; these fibres are characterised by a good strength at break for albeit moderate Young's modulus. Bamboo fibres display the highest performance in terms of strength, ranking above those of flax and alfa. Although these fibres possess relatively low stiffness, their high strength is explained by their elongation at break which is above that of the other elementary fibres, the average elongations of the fibres of the first group being between 0.8 and 4.5% and that of the second group between 3 and 10%. These differences in terms of elongation can be explained by substantially higher MFA values (Table 1) in the case of wood and cotton but also by a lower cellulose content for bamboo (see Table 3); these two parameters probably induce more slipping between cellulose microfibrils and a lower stiffness inducing an improvement of the elongation. Despite a reduced stiffness it allows to raise very interesting strength. Thus, as was the case for morphological properties of plant fibres, comparison of plant fibre mechanical properties highlight moderate to huge (more than 100% of the characteristic study) differences from one plant species to another. This highlights the difficulty to generalise a common typology for the entire panel of plant fibres, with each fibre having its own specificities and performances.

Table 3 shows the biochemical composition of the plant fibres.

Table 3

As for the morphological and mechanical parameters, important differences in composition arise between plant fibre elements, both in the bundles including the middle lamella and on the cell walls of individual fibres. These characterisations, though reflecting all contents of cellulose, hemicellulose, pectins or lignin, have not always been carried out in the same way, and may be conducted on different stages of fibre extraction and processing (such as on retted or un-retted materials), which can modulate the biochemical composition widely. At the analytical level, the

extraction time and solvent concentrations may be different, and comparison is therefore biased because most of these analyses were performed by the Tappi [142], van Soest [143] methods or by specific protocols derived from these [144,145]. However, we can note that all these characterisations were performed on fibre bundles rather elementary fibres. Significant differences can be observed between the plant species as regards the contents of cellulose and lignin. The lignin content can be governed by the genetic pool of the plant, but is also be controlled by cropping parameters as is the case for flax which is pulled out before its lignin content increases to facilitate the extraction of fibres from the plant. In terms of biochemistry, there exists a wide range of cell compositions which does not consider the different plant cell walls as equivalent. Some classifications nevertheless attempt to group them in large families; according to Mikshina [146], plant fibres can be categorised into two broad types, the xylan-rich and the gelatinous ones. The xylan type are secondary cell walls characterised by helical orientation of cellulose microfibrils, with predominance of xylan in the non-cellulose matrix, and a high degree of lignification.This is for example the case of wood cells or bast fibres such as kenaf or jute. The second family type (gelatinous) is of thick secondary type cell wall present only in fibres with high content of cellulose (up to 90%) and of high degree of crystallinity; it concerns for example tension wood or flax fibres.

2.2.2. Classical representation of plant fibres

In the literature, the plant cell walls and fibres are generally defined by a primary wall, a secondary wall, and lumen. The secondary wall is usually described in the form of three sub layers S1, S2 and S3, the S2 being the predominant layer. The S2 layer is made of cellulose microfibrils embedded in a polysaccharide matrix and oriented along the axis of the fibre with a MFA having generally a fixed value. Thus, whatever the species of plant, the fibres are generally presented in this architecture and illustrated by a scheme, similar to Figure 8 [147].

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Figure 8

This simplistic presentation allows to present in summary form the overall architecture of plant cell walls but does not reflect necessarily the reality. Indeed, whether by the number of layers, the orientation of microfibrils, the helix direction, the contents of cellulose, polysaccharides or the size of the lumen, the different plant fibres all have specific characteristics and it seems very difficult to want to assimilate them in a elementary ideal model structure.

As we will see in the next section, they all have very specific morphologies and ultimately have little in common. It is therefore necessary to clarify this to avoid generalisation that would overlook the specificities, advantages and disadvantages of each one.

2.2.3. Diversity and complexity of the plant cell walls

As we have seen previously, the various plant fibres have specific morphological attributes for each of them and it is not possible to consider them as one fully identical. Figure 9 shows longitudinal images of the different fibres listed in paragraph 2.2.1.

Figure 9

This overview confirms the morphological variety of these fibres. The sizes of the fibres or bundles are hardly comparable and in some cases (i.e. coir) we can see that the individualisation of cells is very delicate, the bundles can be here considered as the basic unit. One can also note significant disparities in terms of surface. Indeed, some fibres such as cotton, linen or kapok having surfaces virtually free of impurities while alfa, coir, or hemp have rough surfaces and middle lamellae residues. This may be the result of a low level of retting, either

due to a significant lignification or difficulty to extract the fibres, caused by unsuitable scutching or mechanical means poorly adapted to stem structure. These aspects of surfaces will of course affect the interfaces within composites. In special cases, we can also note the twisted forms of fibres (cotton) or the presence of pits that function as valves (wood); the offer potential resin flow paths for entry in and out of cell lumen during the processing of the composites.

Figure 10 shows the cross sections of these fibres. One can see some similarities between several plant fibres.

Figure 10

For example, coir and abaca fibres are assembled into bundles in which there is a lacuna. In this case, we are dealing with short fibres that will be difficult to individualise. Bamboo also has a particular structure; it is a herbaceous monocot and fibres vessels are dispersed throughout the stem cross-section, albeit at locally higher densities towards the periphery. Thus, these fibres require significant energy to be extracted from the plant. Important differences in shapes may also be noted. Some fibres such as flax or jute have regular and homogeneous shapes, others being more elongated or more disparate shape; this is particularly the case of hemp or cotton. Finally, lumen sizes are very different between the fibres. They only represent a few percent of the fibre section for flax [56], hemp [21], ramie [57] or bamboo [48] but the size of the cavity may be 20 to 30% of the overall section for sisal [56], jute [56] and abaca [45,99] or 60 % and 90% for kenaf [84] and kapok [82], respectively. Concerning wood, lumens may vary from 2 to about 70% [156] depending on the nature of the cells and the types of woods.

2.3. Origin of the structural differences

In this section we will try to shed light on how the structural differences observed among the different species of plant fibres arise. For this, we will focus first on their function in the plant,

secondly on the potential role of their environment during growth (thigmo-morphogenesis), and lastly crop parameters that may have a significant, and sometimes undesirabe, influence on fibre properties.

2.3.1. Importance of the fibre origin (stem, leaf, fruit, seed, wood) and role in the living plant

Let us initially focus on the specific function of the fibres. As we have briefly described previously, plant fibres can be in the stem, the leaves or surrounding fruits or seeds. The location has a direct effect on the morphology and properties of fibres due to their function in the plant. Take for example the case of coir fibres which are located in the mesocarp of the fruit and play a protective role in shock when the nut falls. As we have seen previously, these fibres are assembled in tube bundles of a few hundreds cohesive fibres [53,75], with extra lignified cell wall layers; they also have a large lumen [53] that allows them to show strong impact absorption capacity that results in high elongation at break, compare to other plant fibres. Thus, despite moderate tensile performance, coir fibres exhibit specific properties that allow them to fully perform their protective function in nature.

This is also the case for seminal hairs such as cotton or kapok; they surround the seeds and are intended to promote their dissemination by wind; in contrast to other described fibres, they are not sclerenchyma cell types. Cotton fibres are elementary elongated cells formed from the seed coat protodermis (immature epidermis). Dozens of seeds are formed within a boll, each ovule producing between 10 000 to 20 000 fibres with a length of 10–60mm [159]. Due to their function, they do not need strong mechanical performance but must be thin, light and relatively long; cotton fibre can be characterized by its fineness, its high cellulose content and its specific helical shape conducive to entanglement of fibres that will allow the formation of a cocoon around the seed and facilitate its transportation. This twisted and original shape is due to the stress release occurring at maturation; at this step, the fruit capsule opens, and the cylindrical fibres dehydrate and collapse to ribbon- like, twisted structures [159]. In the case of kapok, the biochemical composition of the walls is very different with greater lignin content and the hollow morphology of the fibres gives them a very small bulk density which also promotes transport of

the grains by the wind [82].

Other fibres such as abaca, alfa or sisal come from the leaves. They are characterised by relatively moderate mechanical properties and quite short lengths. They have no dedicated structural properties but still contribute to the mechanical strength of leaves and generally have relatively high elongation at break to allow to collect the stresses and strains caused by wind or rain. These fibres are assembled in cohesive and lignified bundles and play a transportation role of sugar produced by photosynthesis which means that they have developed lumens of sufficient size, lumen being the vestige of living cells' cellular metabolism.

Finally, the last category of fibres that we have chosen to detail here is the group belonging to supporting tissues located in the stem, those fibres strongly contribute to the stability of plant stems. Among these we can find species like 'wood', jute, ramie, hemp or flax. However, again, it is appropriate to make distinctions between group's members because these fibres will not show the same performance in particular due to the geometry of plants, but also of the fibres itself. The plant geometry may be addressed by the slenderness factor of plants that characterizes the ratio between height and stem diameter.

Figure 11

The work of Niklas [161–163] has particularly helped represent these specific characteristics in the form of graphs. Figure 11 shows the relationship between the height and the diameter of a large number of grass and trees. It represents both experimental and modeled values by varying the equation parameters modeling the relationship between diameter and height. The red dot represents the case of flax and underlines the extraordinary slenderness factor of this plant. Thus, flax stems possess particularly slender stems whose stability can be considered to be close to or greater than the theoretical limit established by Niklas' work. This is caused by the specific structure of the stems, with a significant number of peripheral fibres [59,164] but also by the mechanical performance [165] of these walls and by their length [166], substantially

greater than most of the bast fibres. The latter is due to the ability of these cells to form a plurality of nuclei [146] and therefore to be able to along very significantly during the intrusive fibre growth [64,167]. Thus, among the bast fibres, some like hemp, ramie or flax possess this polynuclei character; this is not the case of jute which, for this reason, exhibits lower fibre lengths [57].

2.3.2. Thigmomorphogenesis

This domain embraces the growth responses of a living plant to external stimuli like mechanical forces. Variations in fibre mechanical properties could be explained by the structure of the fibre and the biochemical composition of its wall [20,168,169] and could be due to the varieties in the gene pool (e.g. of flax [170]), but they could also be influenced by environmental stimuli mainly induced by rain or wind [166]. The most common features of thigmomorphogenesis on plants are a decrease in vertical growth and an increase in radial expansion [171] but it also has an influence on the quantity and stiffness of strengthening tissues [172,173]. Furthermore, the stimuli frequency has an impact on the plant acclimation as well as on their specific responses, particularly on the increase of the stem diameter [174]. If stress occurs at air level (reduction of illumination, leaf area reduction), the plant responds by developing its air system, and if the stress comes from the ground (water stress, nutrient deficiency), root development is preferred [175,176].

Amongst other indicators, the involvement of calcium in the early events of exterior stimuli sensing and transduction was found [177,178]. In the case of flax, Verdus et al. [179] evidenced that the number of meristems produced is strictly dependent on the intensity of the environmental stimuli received; the meristems production being governed by calcium depletion signals. On *Arabidopsis*, Braam et al. [180] showed that the TCH gene regulation and expression is a response to environmental stimuli and could lead to an increase in xyloglucan crosslinks with cellulose microfibrils and hence cell wall reinforcement of non-growing cells stimulated by touch or wind. In wood cell walls, xyloglucans play a linking role, between the S2

and G layers [181]; in flax cell walls, xyloglucans are part of the non-cellulosic polymer matrix and are mainly present in the primary wall [182].

During the flax growing period, environmental stimuli are mainly due to the sun, wind and rain, which can induce plant lodging. The boundary conditions, i.e., the anchorage quality and the soil behavior are also preponderant parameters for plant stability and the lodging is highly influenced by the stem stiffness, the environmental stimuli and especially the extra water weight. Consequently, the distribution of water drops on the plant increases its mass and, with windy conditions, the risk of instability becomes even more significant. The work of varietal selection aims to develop new varieties to increase the production of fibres or seeds but also concerns the behavior of lodging or disease resistance, which are primordial parameters in order to ensure a sufficient income for the farmers. A previous work [59] evidenced that the lodging stability of flax was correlated to the supporting tissues mechanical properties. The lodging stability criteria, which could be optimised by varietal selection, could be assimilated to an indicator of the flax fibre's mechanical performances. Furthermore, the varieties having a high lodging resistance generally exhibit a high fibre yield [59,183]. According to Menoux et al. [166] the fibre aspect ratio (length divided by diameter) is also a good indicator of the plant's lodging tolerance, underlining the fibre's role as supporting tissue.

2.3.3 Cultural and climatic parameters

Due to the lack of literature data on the impact of cultural and meteorological parameters influencing the entire panel of plant fibres embraced in this review, this section mainly focusses on flax and hemp for which data is available. The stem and fibre morphology, and consequently the plant's stability are strongly linked to a cultural parameter: the seeding rate. Indeed, the number of ramifications, leaves, the quality of rooting, as well as the nutrients or water availability are key parameters for the stem's stability and development. For flax, in order to reduce the lodging risk and maximize the fibre yield, the recommended number of plants is approximately 1500/m2 [184]. In general, an increase in the seeding rate induces a decrease of the stem or fibre length [185] and diameter, the number of ramifications [186–189] or capsules

[190] is reduced, whereas the straw yield increased [185,186,189]. The increase in the plant's density generally induces a yellowing and a decrease in the number of fibres, especially at the bottom of the stem. In this case, the risk of lodging is increased [185,188] due to the lower cell wall thickening and poor retting quality. Nevertheless, in the cases of poor or dry soil, a high seeding rate could be a solution to facilitate the plantlet emerging due to collateral help. Also agricultural management is well known for strongly influencing plant development and associated yields [191] as illustrated by the impact of the seeding rate on the chemical composition of bast fibres [192].

High seeding rate helps promote competition between the stems that will stretch to win in sunshine and optimize the creation of support fibres. Studies on flax have found that for a density of 1600-2000 plants / m^2, the average diameter of elementary fibres was between 14 and 15 microns when it was equal to about 18 microns in average for a density of 300 plants / m^2 [193]. In a previous work [22], also on flax, the Aramis variety was studied with 4 different seeding rates (1200, 1500, 1800 and 2500 seeds/m²). The results indicate the significant impact of the seeding rate on the stem's morphological parameters; its increase induces a progressive decrease of the scutched fibre length and of the stem diameter. At the same time, the higher seeding rates obtained improved the scutched fibre's yield (+11% between 1200 and 2500 seeds/m²) but, conversely, induced a drop in the elementary fibre's tensile properties (Figure 12) and in the flax stem's lodging stability, mainly due to the large decrease in the stem's diameter. Those data show that a compromise must be found to optimize the fibre yield, the mechanical performance and the plant's stability; it underlines the relevance of using a conventional seeding rate, close to 1700 seeds/m^2.

Figure 12

Depending on the climatic conditions, the degree of maturity could be different between the outer and inner fibres [194]. In the same way, thickening differences could occur along the

stem, due to climate variations between the first and the last thickened fibres [59]. Thus, according to the variety or the growing conditions, the cell wall development could create some plants with various architectures, fibre structures or mechanical fibre properties. Moreover, the thickening of the fibre areas could vary, inducing stems with highly contrasted mechanical performances [195]. Meteorologically speaking, the culture of flax needs a wet environment with a regular alternation of rain and sun. Thus, a drought period or an excess of rain would stress plants, reducing the growth, increasing the stem diameter, and affecting the fibre formation [196]. Flax does not grow below 5 °C and the growth is disrupted above 28 °C. Based on these observations, an equation (Equation 1) has been created in order to control the accumulated temperatures received by the plants during their growing:

$$\sum \theta°C \ corrected = \sum_{i=1}^{n}(\frac{\theta max_i + \theta min_i}{2} - 5) \qquad (1)$$

It was established that the speed of development of flax fibre is proportional to the sum of cumulative temperatures by the plant; thus, accumulated temperatures are a monitoring indicator of the different stages of growth and are checked before harvesting as well as the germination rate [184]. The plant rising up and fibre maturity occurs generally around 50 and 1000 cumulated degrees, respectively. During the growing phase which occurs during approximatively 100 days [194], the climate remains an unpredictable factor. Drought and excess water are climate scenarios to consider in order to know the impact they can have on the development of flax fibres. Both sufficient data describing a climate according to Kottek [197] are temperature and rainfall.

Milthorpe studied in 1945 the influence of a lack of water on the development of flax stems and fibres [198]. Under the effect of water stress, the plant responds by setting up several defence mechanisms. First, it was observed that drought reduced growth velocity resulting in a lower height of stem. Then, in order to limit the loss of water by transpiration, leaf size is also reduced. As regards impact on fibre development, drought reduced the percentage of fibres and reduces their average diameter. If the number of fibres per bundle varies depending on the position along the shaft as well as dry conditions, the number of bundles along the stem itself remains

roughly constant. Furthermore, it has been observed that drought reduces the filling of the fibres. These observations were confirmed by Chemikosova et al. [196] by studying two groups, a control group and a water-stressed by cessation of water supply for 2 days. The group suffering water stress had a lower elongation, exhibiting a 16% decrease in the number of fibres per section and a small reduction in the percentage of fibre in the stem. Moreover, a wide variation in the fibre length along different parts of the stem due to drought and delayed elongation during this period was shown. In addition, the study found that the drought impacts on the composition of the fibre walls. Indeed, the ratio of galactose / rhamnose decreases when the fibres have undergone drought. This ratio measures the length of branching chains of polysaccharide rhamnogalacturonan- I (RG-I) related to pectic acid polysaccharides, and comprises the matrix embedding the cellulose microfibrils. However, according to Chemikosova et al., [196] it is possible that a change in the ramifications of this pectin makes changes in the interactions between the microfibrils through the matrix impacting the mechanical properties of the fibres. In another paper, Belyak et al. [199] conclude from their tests that drought has consequences for fibre yield while a surplus of water does not compromise fibre performance after harvest, as long as there is no lodging.

Temperature and sunshine are also important parameters. In 1945, Milthorpe took into account the influence of the shade and therefore a lack of sunshine on the development of flax and flax fibres [198]. The lack of sunlight has been considered as a factor most limiting to plants that lack of water. The height of the plant, the fibre percentage, fibre size and speed of development of the plant were all diminished by the lack of sunshine. In 2013 and 2014, Lefeuvre et al. [60] studied the tensile properties of 13 batches of flax fibres (Marylin variety) grown over 4 years under 4 different climatic conditions ; two of them were characterized by a rain deficit, one very rainy and the last considered as normal condition. Interestingly, it was found that tensile properties of elementary flax fibres were reproducible despite drought or an excess of water (Figure 13). In this case, fibres were extracted from the same part of the plant (middle of the stem)

Figure 13

Indeed, the mean values of Young's modulus and strength at rupture of elementary fibres ranged from 47 GPa to 66.2 GPa and from 853 MPa to 1183 MPa, respectively. The dispersion of the tensile parameters values was reduced compared to the values previously reported in the literature [165]. ANOVA statistical analysis showed that the average tensile properties of Marylin fibres were relatively constant despite the year of cultivation. Considering flax fibre as a composite per se, biochemical data highlighted a constancy of the cellulosic percentage (around 84%) and the preponderance of alkali (representing the coating interphase) over the acid (considered as the composite matrix) extracted- matters (ratio range 1–1.7). This ratio was in favor of the establishment of bridges between microfibrils, by neutral hemicelluloses, inducing performing mechanical properties. Some variability was observed in the content and composition of the alkali extract of the 2011 samples which underwent to the most drastic drought stress but within a tendency which would reinforce the tensile properties of the elementary fibres. In comparing four years with very different climates Casa et al. [190] studied the influence of climate in Italy. The year 1996 was dry, 1997 was wet and the years 1995 and 1998 were considered to be intermediate. The main factors considered were precipitation, temperature and the number of seeds planted per m^2. It was found that relative to the two other factors, the temperature generates the greatest impact on the plant. Indeed, growth is slowed down if the temperature drops below 0 °C after emergence or if it is too high (> 28 °C) during the cycle. Zajac et al. [201] studied eight varieties of flax over three years. They concluded also that the ambient average temperature has the greatest influence on the development of the plant, especially at the emergence period. The results of scientific experiments are consistent with the cultural practices of farmers since it is the temperature that is raised every day.

2.4. Fibres properties: the most influential endogenous parameters

In this section, keeping mind a final objective of composite reinforcement, we will focus on the link between cell wall parameters and morphological, biochemical and microstructural fibre properties.

2.4.1. Proposition of synthesis schemes

Figure 14 provides schematics representing 8 different species of plant fibres.

Figure 14

These schematic representations are made using CAD software (Solidworks©) and consequently, simplifications were done. For example outer or inner edges are idealized; on real cell walls, these can be more complex and the fibre or lumen shape can vary with fibre length. One can see that major differences in morphology exist. Different patterns are presented, taking into account the real scale of the fibres according to the average diameter values encountered most frequently in the literature (Table 1). Only cell walls whose precise structures were available in the literature [1-8] have been represented here. Firstly, one can notice that in terms of dimensions, very important differences exist between plant fibres; bamboo fibres have a mean diameter of about 10 to 12 microns while those of wood commonly reach sizes of 25 or 30 microns. Furthermore, the general structures of fibres are also very different; some have cylindrical geometries, e.g. kapok or bamboo, others hexagonal like flax or rectangular like wood or kenaf; for other species of plants such as hemp or cotton, the shape of the fibres can be likened to a slightly squashed ellipse. Apart from this general trend, the volume occupied by the lumen can also vary greatly from one fibre to another and greatly influence the mechanical properties, especially the breaking behaviour, or the fibres apparent density. Thus, the fibres that have the highest solid fraction are those that play a role in supporting tissue in the stems; this is the case of flax, hemp or cell wall tension wood. For these fibres the lumens occupy only a few percent of the fibre cross-section surface [3,9,10] while for

the walls do not have a structural role as kapok or kenaf for example, the surface fractions occupied by the lumens can reach between 45 and 80% [11,12]. As we see in this schematic summary, due to the major morphological differences between the presented fibres, it is not possible to consider them as simply possessing similar tubular shapes; whether by the shapes and sizes, they all have their specific characteristics that enable them to better fit to their functions in the plant. Over the next two sections, we will specifically focus on these structures and investigate the differences in terms of cell wall layers and MFA.

2.4.2. Focus on the number and structure of layers inside the fibre cell wall

As shown in Figure 14, the different plant fibres have a very significant diversity in terms of microstructure; if one is interested in layers of these walls it is not possible to assimilate them to a simple stack consisting of a primary wall and a secondary wall divided into layers S1, S2 and S3. While this conventional representation is generally valid and useful, the structures of each layer may differ from one plant to another; thus, the arrangement, their size or thickness can be extremely variable.

For example, it is possible to compare the secondary wall of a flax fibre, cotton, wood, bamboo; Figure 15 shows images taken in a scanning or transmission electron microscope for these fibres. One can note, for bamboo and wood, high visible boundaries between the 3 main layers S1, S2 and S3; in literature, anatomical descriptions of bamboo [202,203] show an S2 wall split in different sub layers having varied micro fibril angles and thicknesses; (note that these layers do not appear on these images).

Figure 15

Furthermore, concerning wood, the S3 layer is not always present; it is found that in the case of tension wood or reaction, this layer is generally replaced by a gelatinous layer [207]. In general,

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wood fibres have structures and arrangements that can be very different depending on the position in the plant, or the age or type of wood. If we look at the structure of flax or cotton fibres (Figure 15), the multi-layer appearance is visible here, but rather than having just layers S1, S2 and S3, many fine layers are visible. In the case of flax, they correspond to successive deposits of cellulose when filling walls during the intrusive development phase of cells; this process will be detailed in Section 3 of this work. In the case of cotton, the layers observed on the image also correspond to the formation of the cellulosic wall but, unlike flax or hemp, this is deposited during cell elongation [159]. As with flax, it is difficult on the image to identify the layers usually described on this fibre and schematically shown in Figure 14. Moreover, the structure of cotton fibres appears very different from other tissues presented; it appears as a succession of non-cohesive stacks. It also is important to clarify that these are not sclerenchyma fibres but are cells formed from the seed protodermis [159]; these cells possess, at maturity, a substantially larger proportion of cellulose compared to other plant fibres.

Morphologically speaking, major differences in terms of layer thicknesses are reported between plant fibres, even within the same species. This is for example the case of wood: the thickness of the cell walls is very heterogeneous and depends on the species but also the cell growing periods. In temperate regions, those cells produced by meristem in the early season appear to have much thicker walls than those formed in the summer, the need for conduction of sap being much higher in the spring. Remember that these tracheids play a structure-supporting role in the plant but also of conduction of sap. These variations in wall thickness can also occur for annual plants such as flax; in this plant, the cells are filled with cellulose between March and June. The cells at the bottom of the plant, are typically thickened first, however if they face severe weather conditions, it will penalize these cells by stopping filling, leading to thinner wall thicknesses [59]. Generally, significant differences in fibre thickness can also be caused by the phenomena of thigmomorphogenesis, environmental stresses being able to influence the outdoor plants structure. Artificially supported plants will need less rigidity to remain stable and its fibres are also generally less filled by cellulose [171,180]. Besides these parameters related to growth, patterns of Figure 14 also show that the walls thicknesses are highly species-dependent , and function-dependent. For example from fibres with the finest walls such as

kapok, the fibres act as seed dispersal and require very low bulk density; cell wall thickness is also reduced for kenaf or normal wood whose fibres are conduction tissues. In contrast, flax or hemp exhibit much greater wall thickness due to their role as supporting tissues.

2.4.2. Microfibrillar angle

The MFA characterises the orientation of the cellulose fibrils in the secondary walls of plant fibres with respect to the axis of the fibre. Given the nanometer-scale size of these fibrils, they are difficult to observe. However, Atomic Force Microscopy (AFM) [208] or electron microscopy [209] allow in some cases to view this orientation as we can see in Figure 16.

Figure 16

However, it is difficult with these methods to obtain accurate values of the angles, especially with AFM, because of the lack of reference in relation to the axis of the fibre, due to the high magnification of the studied areas studied. The use of XRD enables a better understanding of crystalline and molecular orientation and to obtain suitable values of MFA. By coupling XRD and tensile experiments it is possible to understand the impact of a mechanical measurement on amorphous and crystalline part of fibres. In literature, many authors have used X-ray diffraction (XRD) to explore MFA of natural fibres. Some XRD studies have been dedicated to the knowledge of spider silks; Miller et al. [210] studied the nanofibrillar morphology of spider silk with small-angle x-ray scattering (SAXS) and AFM. In another study, Putthanarat et al. [211] used the X-ray diffraction at large angles (WAXS) to characterise existing angles between the nanofibrils in spider silks. In this paper, AFM photographs were taken to characterize the angles between the cellulose microfibrils and their mean dimensions. These results show that 72% of the crystals are parallel to the axis of the fibres, 14% to + 45 ° and 14% at -45 °. Whole offset peaks (28%) is close to the result calculated by AFM (30%).

On wood, Cave [212] showed that intensity profiles on the 040 plane of cellulose enables a direct measurement of the distribution of MFA in the S2 layer. MFA distributions can thus be obtained. Reiterer [213] has also published work on the determination of MFA on varieties of pines. To estimate the value of the MFA, the SAXS 2D charts were collected for multiple values of the rotation angle (β) of the sample around the longitudinal direction. For each data series, the total scattered intensity on the detector is plotted as a function of the polar angle ψ. The maxima are interpreted as the diffusion lines of directions and plotted as a function of β to estimate the MFA. For the studied fibre batches, the authors identified MFA ranging from 2 to 4°, according to the angle β. In the stem, the resulting angle is less than 5 ° for young wood and equal to about 20 ° for old wood. In the branches, MFA is about 30 ° at the top and 40 ° for lower part. These variations indicate that this angle has a function related to the mechanical stresses of wood.

Reiterer et al. [214] studied the influence of MFA on the deformation behavior of pinewood cellulose. These measurements were made using a video extensometer and showed that the MFA has an influence on the tensile behavior in both the transverse or longitudinal directions. High Poisson's ratios (greater than 1) were obtained for intermediate MFA of around 27 °. However, using X-ray scattering, Keckes et al. [215] showed that cell walls of wood could regain their original state after deformation by a Velcro-type mechanism and that changes in the MFA when applying a tensile strain follow a simple linear relationship with applied strain.

Burgert [216] and Keckes et al. [215] showed that for wood a decrease in the MFA at higher tensile stresses. It is therefore likely, as pointed out by Baley [8] that during a tensile test, cellulose microfibrils are realigned at the beginning of experiment, which inevitably leads to a reduction in the MFA. Numerical investigations were conducted in this direction by Trivaudey and Placet [217] on hemp fibres. They showed an evolution from 11 to 7.2 ° of the MFA of a hemp fibre subjected to a force of 0.5 N. In the same way, in line with the work of Joffre et al. [218] and Neagu and Gamstedt [219] on wood and Placet et al. [66] on hemp, we could assume different mechanical behaviours and properties of fibres, depending on whether they are free or embedded into a polymer, without any possible rotation and consequently potential changes in

the MFA values. According to these authors [66,218,219], a plant fibre containing an S2 layer with a MFA of 10° would have a stiffness of about 30 GPa assuming free rotation, whereas the same rigidity would be close to 60 GPa if fibres are un-twisted.

The microfibril angle can evolve during a tensile test but it may also be different for different fibre varieties or species (Table 1). Salmén [220] grouped values of MFA measured on different wood fibres, which differ in particular by their cell wall content or the proportion of fibres from the layer S2; demonstrating significant differences in stiffness, depending on the measured MFA. Similar representation was proposed by Eder et al. [221] by synthetising the evolution of tensile modulus of both elementary fibres and wood samples according to their MFA (Figure 17).

Figure 17

These differences are also noticed in bast fibres. Indeed, flax and hemp, which have good mechanical properties, have MFA between 8 and 11 ° [217,20], while sisal, displaying lower mechanical stiffness and strength, has a MFA of about 20 ° [90]. This trend is even more pronounced for wood and cotton, which have large MFA (between 20 and 40 °) and low mechanical properties [220,222,223]. Relationship between elementary flax fibre tensile properties and MFA values were studied on 9 varieties by Bourmaud et al. [20]. An interesting relationship was found between the MFA and the flax fibre mechanical properties, as it exists for wood but within a much wider range of MFA values [220]. A strong negative correlation exists between the MFA and the flax fibres Young's modulus (r2 = −0.75). Nevertheless, in this work, MFA have been obtained on unstressed fibre bundles whereas the Young's modulus has been calculated on the second part of the stress–strain curve of elementary fibres. The determination of the stiffness in the first part of the stress–strain curve has little meaning due to the progressive loading of the micro fibrils occurring at the beginning of the test; in this case, the values that were obtained would not be representative of the real properties of the flax fibres.

Gindl and his team [224,225] published some work on the characterisation of cellulose fibres by X-ray scattering. They observed preferential orientation of cellulose microfibrils in the direction

of the force applied during a tensile test. Comprehensive reviews of literature on this subject is available in [212,226]. It has been shown that the tensile mechanical properties of wood fibres depends on this MFA [212,227] and that this angle can be obtained by X-ray diffraction techniques at small angles XRD [213]. Martinschitz et al. [54] have focused on the characterisation of tensile-loaded coir fibre by small-angle X-ray scattering (SAXS). The evolution of the spectra peak corresponding to the 200 plane of cellulose indicates a decrease in the MFA from 43 to 27 ° at the max of the stress. An increase in tensile stiffness was observed, which can be interpreted as an alignment of cellulose fibrils along the axis of the loading. However the slope remained similar in the elastic portion. In cycling tests, the MFA values vary according to the tensile profile; they decrease during the loading phase and remain stable or slightly increase during unloading without ever reaching the values before unloading. This behavior is similar to that already observed in wood cellulose fibres [228]. Unlike wood, it is shown here that the coir fibres do not need to be saturated with water so that the values of microfibril angle gain relative stability during loading-unloading cycles.

These different works clearly highlight the influence of MFA, both on the fibre mechanical properties but also on their behavior during a tensile experiment.

2.4.2. Importance of biochemical composition and link with mechanical properties

As described previously (Figure 8), for the main plant fibres in use as polymer composite reinforcements, the stiffness of the secondary cell walls is the result of the presence of highly-oriented bundle of cellulose microfibrils within the S2 layer. In case of flax, tension wood or hemp fibres, these mesofibrils represent more than 80% of the weight and together with the non-cellulosic polysaccharides (ncps) (in which the mesofibrils are embedded), they form a high performance composite. Thus, cellulose is the major constituent of flax fibres; it is also one exhibiting the most interesting mechanical properties. Based on the work of various scientists, the Young's modulus of crystalline cellulose converges towards about 134-136 GPa [105]. The poor mechanical properties of the other components (2 GPa for stiffness of the hemicelluloses [43] in dry atmosphere (12%) and 0.2 GPa in an ambient atmosphere) allow them to have only

a marginal influence on those plant fibres. The level of cellulose contained in the flax, ramie or hemp cell has arguably a direct impact on the mechanical properties of the latter, but it can't be considered as the only factor influencing these properties in light of the structural organisation of the fibres. Structure of cellulose as well as its degree of crystallization are additional important parameters influencing mechanical performances. Some authors have observed the impact of proportion of cellulose on mechanical properties [229] and defects or dislocations could be considered as weakness points of the plant cell walls [230]. It appears that the fibres which have the highest level of cellulose, such as flax or ramie, are those which possess higher mechanical properties. However, this is not always the case; and cotton, although with a high cellulose content, displays very low tensile properties. Cellulose rate is not solely responsible for the mechanical capabilities of plant cell walls. Besides the MFA that is know to impact on the mechanical performance of plant cell walls, different theories, based on the work of mechanical engineers or biologists, enable the arrangements of the different cell wall constituents to be explained.

Hearle [231] showed that the cellulose mesofibrils are closely linked to the amorphous polysaccharides and form a non-covalent network with the hemicelluloses (principally glucomananes and galactanes according to Gorshkova & Morvan [232]). The hemicelluloses are bonded to the cellulose mesofibrils by weak hydrogen bonds which, on account of their large number, create strong associations with the cellulose. Part of the hemicelluloses can form inter-cellulose bridges and/or entanglements (and untangle) with the pectic matrix. Beyond a certain shear stress threshold this network can fail due to breakage of the hydrogen bonds between the constituents. Other studies on wood have revealed a stick-slip (Velcro®) mechanism in the secondary cell walls [17,233,234]. According to Burgert [216] and Keckes et al. [234], the Velcro® mechanism is partly reversible after loading and other hydrogen bonds between cellulose and hemicellulose will be built elsewhere. Altaner and Jarvis [233] propose a slightly different model in which, in addition to hydrogen bonds with cellulose, the hemicellulose chains can make bridges or loops with cellulose mesofibrils.

Comparative work on the fibre structure of different varieties of flax [235] have shown stiffness differences related to cellulose content in the cell walls; the varieties with the highest cellulose content were represented with cellulose fibrils that are closest together and a less well-developed matrix between the fibrils. The bridges between glucomanane chains have been proposed to explain the stiffness differences observed [235]. In flax fibres other components such as arabinogalactan proteins (AGP) or proteins rich in glycine (GRP), and □-1-4 galactans have also been proposed to play the role of « hemicelluloses», i.e. of compatibilisers between the cellulose mesofibrils and the pectic chains (RG-I) to which they are linked, representing a true interphase between the matrix and the cellulose and ensuring cohesion of the system [235,182,232]. This configuration can be reinforced by the presence of homogalacturonans which will consolidate the interphase between the galactans and the pectic matrix [235,232]. This analysis was based on models of in vitro interactions studied by Zykwinska et al. [236] and primary cell wall models elaborated by Cosgrove [237].

Figure 18

A schematic synthesis of the structure of the S2 cell wall is proposed in Figure 18. Recent studies [20,103] have shown the importance of the organisation of the plant cell-wall components and their structure in the mechanical performance of the fibre. More than the quantity of cellulose, which is present in sufficient amounts to ensure good performance, the ratio between the structural polysaccharides (EOH) (hemicelluloses with high polymerization degree) and matrix (EH) (low polymerized polysaccharides) within the S2 layer present a high correlation with the stiffness of flax fibres.

Figure 19

Regarding previous data on Hermes and Oliver flax [238], which dealt with the impact of the presence of pectic acid – and especially of homogalacturonan – in EOH, a correlation between the content of the uronic acids (UA) and the mechanical properties was investigated [20]. Interestingly, a positive correlation has been found – especially for EH – between the UA percentage (relative to the mass of polysaccharides) and the strain at break.

The larger the quantity of UA in the matrix, the greater the sliding between microfibrils during tensile loading. Moreover, as observed in Figure 19, the ratio UA EOH/EH shows a strong positive correlation with the tensile module ($r2 = 0.85$), proving, through the example of flax, the strong link between biochemical composition or structure and mechanical properties of flax cell walls.

2.5. From the plant to the fibre: retting and extraction

2.5.1. Retting step

The aim of retting is to facilitate the extraction of the fibres by the degradation of the cortical tissues surrounding the fibre bundles. In the case of European flax, initially carried out with water in routers, it was progressively replaced by dew retting from the 1950s due to environmental considerations. Indeed, water retting had the advantage of producing a high and reproducible fibre quality, however this method vanished in the EU because it left large quantities of polluted water [239]. Land reclamation was favoured by farmers in order to limit water eutrophication. The stems are torn off and then deposited on the field in the form of swath (flax sheets of a width corresponding to the height of the stems). These different steps (uprooting, turning and winding) have been totally mechanised in order to limit their cost. The retting time can vary from one to several weeks depending on the climatic conditions and corresponds to a semi-controlled degradation of linseed stems [240]. This is the first step in the normal process of biodegradation of the plant.

During retting, flax stems are colonised by fungi and bacteria. These microorganisms secrete enzymes which accelerate the degradation of the polysaccharides of the plant. Enzymatic activity favours degradation of pectins [23,241–245] and a conjugation of wet and mild weather will promote the development of microorganisms (fungi, bacteria) secreting degrading (or hydrolases) enzymes such as polygalacturonases or xylanases. The pectins of the middle lamellae of the cortical parenchyma, the epidermis, the xylem and the bundles of fibres are gradually degraded, which makes it easier to extract the bundles during scutching. The fibre bundles are also divided [239,246] (Figure 20) and Sharma et al. [247] showed that the limiting factor of retting is the degradation of homogalacturonans, in particular for those located in the epidermis.

Figure 20

Retting is an important step for the production of flax fibres, since it has an influence on their quality. Homogeneous retting favours the production of fine technical fibres [248] [21]. Meijer et al. [23] observed that leaving the stems to fade before retting allows a more homogeneous retting. Tedding would result in micro-holes in the bark of the stems facilitating the passage of microorganisms. However, dew retting is climate dependent and difficult to control. If the climate is too dry, the stems will be sub-retted. If the climate is too wet, they will be over-retted following the secretion of a second type of enzyme (cellulase) attacking the cellulose making up the fibres as shown on hemp by [249]. Farmers define a degree of retting by subjective observations using organoleptic criteria. Thus, the homogeneity, the color, the resistance to a hand tensile test or the divisibility are all criteria evaluated in the form of a quotation. The ease of fibre extraction and the cleanliness of the fibres are also observed. In order to quantify the retting, Sharma and Faughey [248] did a comparative study of existing subjective and objective methods. The study made it possible to establish a link between several objective criteria and the quality of the technical fibres. The variation of the pectin content during the retting process and also the amount of pectins initially contained by the plant before peeling are key criteria. As

a result, retting is dependent on the stage of development to which the flax is pulled out [23]. After flowering, the flax begins its phase of maturity then of senescence during which the percentage of lignin increases gradually until the death of the plant. The lignification of the stem makes retting and scaling more difficult. Meijer et al. [23] observed that retting is faster when pull-out is done during flowering. However, at the level of a stem, the lignification of the inter-fibre or inter-cellular junctions is not the same at all the heights, making homogeneity through retting difficult. Indeed, the diameter of the bottom of the stem is wider and the junctions more lignified with respect to the middle and top of the stem. Schünke and Schwalen [250] reduced the time to ashore by 5 days by crushing the stems and spreading suspensions of fungal and bacterial spores. Finally, the variety is also a parameter to take into account since some varieties may be easier to turn because of their lower levels of pectins in the adjoining lamellae. The degree of retting is thus a complicated parameter to be controlled. It determines the quality of the final fibres and also scutching productivity.

In Europe, dew retting is commonly used for flax but it is also used for hemp in order to allow the fibre to be separated from the woody core. The traditional method to separate the fibres from the plant is to cut and leave the hemp stems on the field, where they are soaked during the night by the dew, allowing natural bacterial degradation to take place. Under these conditions, microorganisms grow and produce enzymes, which degrade pectic substances, and the cortex fibres are progressively disassociated into fibre bundles and sub-bundles. As underlined for flax, dew retting needs constant monitoring to ensure that the wood and bast fibres separate and provide a good fibre quality. Nevertheless, this process does not need excess watering and it is relatively inexpensive. For hemp, water retting (or pond/river retting) is still widely used in Asia. This process, if well controlled [249], produces a much higher quality with more uniform fibres. In this process, fibres are extracted by a controlled warm- water retting procedure, which is an effective method that avoids extreme weather situations that may come from field/dew retting. If water retting is conducted in a controlled environment, microorganisms or enzymes can be added to the water to aid the retting process to produce very high-quality fibres that retain their high mechanical properties [62]. During water retting, anaerobic bacteria, such as the Clostridium Genus from the soil and stem of plants, develop [251]. They are considered the

primary source of enzymatic activity. The enzymes produced are polygalacturonases, pectate-lyase and pectin-esterases [242]. Water retting, however, causes water pollution, with organic acids and other fermentation products releasing a nauseating odour, which require reprocessing and treatment before discharge into rivers. Despite the quality of the fibres produced, hot water retting was gradually abandoned in Western Europe from the 1970s due to water pollution and the costs of the large quantities of hot water used. Nevertheless, this kind of retting is still used for other plants such as coco, jute, kenaf or sisal.

Extraction of coco fibres is laborious and time-consuming. After separation of the nut, the husks are traditionally processed by various retting techniques generally in ponds of brackish water (for three to six months) or in backwaters or lagoons, which may include sea water. This requires 10–12 months of anaerobic (bacterial) fermentation. Rajan et al. [252] suggest that phenolic substances present in the husk retard the retting process. By retting, the husks are softened and can be decorticated. Environmentally friendly methods for fibre production have the potential to produce a more consistent quality of fibres. Novel developments using a biotechnological approach with specific microbial enzymes have reduced the retting time substantially to three to five days. By using specific (microbial) lignolytic enzymes (laccase/ phenolo-xidase), the fibre surface can be bleached or activated to react more easily with dyes [62]. One can notice that dry milling methods are now developed, they allow to extract coir fibre in areas where soaking facilities are limited or not available.

Regarding jute, kenaf or sisal, water retting is performed over 5 days to 3 weeks, depending on temperature, and requires large quantities of water. The quality of the bast fibres coming from this process is often reduced due to the mixture of organisms and the dirty water. One of the difficulties in the retting procedure is that the thicker parts of the stem take longer to ret than the thinner parts, and, consequently, if the butt ends of the stem are fully retted, the top ends are over-retted and damaged. This can be avoided by stacking the bundles of stems upright with the butt ends in water for a few days, before immersing the whole stem. Correct retting is an essential first step in the production of good-quality fibre. The use of clean water and specific microorganisms has been shown to greatly improve both the efficiency of the retting process

and the quality of the bast fibre [62].

To a lesser extent, enzymatic retting, chemical extraction or steam extraction are also used. These techniques have been developed to overcome the difficulties of dew retting. For chemical retting, the products used in the literature are varied but calcium ion chelators such as ethylene diamine tetraacetic acid (EDTA) are mainly used [247]; they aim to eliminate some pectic substances by trapping calcium which coordinate their polymer chains. Chemical retting has also been studied on jute fibres using 1, 4, and 7% sodium hydroxide to separate the bast fibres from the core [253]. Enzymatic retting is carried out with the aim of eliminating pectic substances and non-cellulosic polymers present in the middle lamellae of the plants; commonly used used enzymes are polygalacturonases [254] or pectinases [127]. Enzymatic retting involves immersing flax straws in an enzyme solution [240,246]. The retting mechanisms are identical to field or water retting. These two types of retting have not been developed on an industrial scale to date. Other methods have been evaluated in order to facilitate the separation of the fibre bundles from the other constituents of the stem such as steam explosion (STEX) [255,256], ultrasonic and microwave treatments [257,258]. Steam explosion is the physical removal of the cellulose and parts from the other glue-like substances which hold the fibres together, it destroys the structure of fibre bundles that the plant has provided. In the case of hemp, Vignon et al. [259] suggests that the tensile strength and modulus of hemp/PP composite were improved after a steam explosion treatment. This method can also be used to separate bamboo fibres; the water contained in bamboo is heated under high temperature and pressure and the pressure is then rapidly released to the atmosphere, so that the water evaporates, shattering the parenchyma inside the bamboo [260].

As detailed in this section, due to the structure or morphology of the plant, different kind of retting are used in the world and despite its eco-toxicity, water retting continues to be used due to its ease of use and the resulting fibre quality.

2.5.2. Extraction processes

After retting, fibres are generally extracted by mechanical processes. This is the case for flax fibres which benefit from the know-how of the textile linen industry, but to a lesser extent for hemp. The scutching allows the extraction of the fibres from the straw by mechanical actions. The producer must find a compromise in order to have an optimal productivity (fibre/ha) while preserving the quality of the technical fibres and limiting the percentage of tows (technical fibres of short lengths). After a grinding action, the straw is crushed between fluted rolls. The second step is a threshing action that begins with the feet and ends with the top of the straw. Depending on the thickness, the degree of retting, the moisture content or the fibre rate of the sheet, the pressure of the mills can be modulated in order to optimise the quality of the extracted fibre. During scutching, the scaling is adjusted in accordance to both the speed of the turbines (90 to 110 rpm) and the speed of the beaters, which can range from 160 to 245 rpm. Whether it is for hemp or flax, it has been found [250] that the scutching of green straw requires more energy than for retted one. Indeed, the more advanced the growth of the plant, the more it is necessary that the scraping force decreases to a threshold corresponding to the end of the plant maturity. The necessary scutching intensity then increases with the evolution of senescence with lignification. The optimum harvest period is at the beginning of seed maturity before lignification is too advanced. The scutching is therefore a delicate transformation step which must be regulated according to the characteristics of the straw at the entry of the line in order to limit the damage of the fibres by the creation of defects [133]. In some cases and to obtain efficient fibre individualisation, scutching can be followed by a hackling step, well described by Salmon-Milotte [261]. The purpose of hackling is to align, untangle and parallelise the bundles of fibres, as well as to remove any undesirable material such as shives or seeds. To a certain extent, hackling makes it possible to divide the fibres within the bundles [262]. After hackling, the fibres are in the form of a ribbon which has the advantage of being continuous with respect to the scutched fibres, which are discontinuous. The hackling efficiency is less than 70% [40] and the production speed can reach 120 kg.h^{-1}, which makes it a relatively expensive process. Tapes resulting from hackling can be used for spinning or preforms for composite reinforcement.

Scutching and hackling process previously described are commonly used for flax, even for

technical uses, but not for hemp. Hemp fibres extracted for paper pulp or composite reinforcement (short fibres) are obtained from specific lines constituted of both milling and cleaning systems. Three kind of milling tools can be used, hammer mill, roller mill or beater. Hammer mills are the most commonly used and industrial lines exhibit generally two successive hammer mills in order to obtain a fibre as clean as possible and without shives [4]. These processes are efficient but more aggressive for fibres than conventional flax scutching.

For bast fibres such as jute or kenaf, extraction is often performed by the same way in specific extraction units called jute mills or kenaf mills located close to the production areas. These little factories have extraction lines with hammer mills. In some cases, stripping the fibre from the stem is still done by hand, after which the fibres are washed and dried. Extensive research has been done on the mechanical separation of the bast from the core on kenaf. Chopped whole stock was used in a process involving a spiked cylinder and an airline cleaner [263] with achievable separation efficiencies of 42 to 48%. It was found that the moisture content was a critical factor in the separation efficiencies and, if controlled, the separation was cleaner and quicker. Regarding abaca fibres, especially in Philippines, extraction remains widely manually done and is called stripping [264]. On the plantation site, the plant stems are de-sheathed, the sheaths flattened, a knife inserted between the outer and the middle layer, and a 50–80 mm wide strip is separated and pulled off all along the length. The plant strip is then scraped by pulling them through or between a wooden block and a serrated knife. The fineness of the stripped fibre increases with increasing serration density of the blade and the pressure used. In other areas such as Central America, Indonesia, and parts of the Philippines, machine-decorticated fibre can be used. This kind of machine consists of a long (30 m) conveyor belt, a crushing press, a pair of crushing rollers, a rope belt, and the decorticator; nevertheless, they induce processing damage that reduces its strength. In contrast, the manually stripped fibre is stronger and more lustrous. The yield of decorticated fibre is only 2–3% of the plant weight [265]; these value are very low regarding the used energy and compared to flax or hemp fibre yield. Conventional yield for long flax fibres is around 25% of the total biomass and 40% if tows are included.

The fibre yield are in the same range for sisal, being between 2 and 5%-wt of the plant and around 800-2200 kg/ha [266]; decortication machines are used to extract the fibre; leaves feed the machine thanks to an endless conveyor and then are crushed by corrugated metal rollers and scraped by a bladed drum rotating at 200-500 rpm. During the scraping stages, important quantity of water (about 35,000 L/ha) is sprayed onto the leaves to assist in separation of the fleshy plant material from the fibre. Wet decorticated fibre is dropped into a tank of water for final washing. After drying, the fibres are brushed mechanically to remove the dust.

Figure 21

Due to the specificity of plant or fibre location, their extraction can be difficult and require high energy processes. This is the case for coir or bamboo fibres (Figure 21). Regarding coir, the coconut is generally manually dehusked, by using machete and hand stripping or with machines that cut through the husk and then peel it off [264]. After this step, the fibre is extracted from soaked husks by wet milling, or defibreing, on special machines called drums, which are arranged in pairs on the same axle. The pair of drums can handle 2000 husks in 8 h, producing 100 kg of bristle and 250 kg of mattress fibres. Other systems, operating by dry milling can be used when soaking facilities are not available. Bamboo fibres can be extracted by using steam explosion, as previously described but due to the expensive cost of this method, a combination of chemical and mechanical processing is generally preferred. Generally, the culm has to be first reduced to smaller particles, which are fed into a refining process where under heat and some pressure, the material is separated into individual fibres [202]. After this step, in case of particleboard production, the fibres are then introduced into a blow pipe where the fibre material is dried and resinated. Most manufacturers use chemical processing with an initial alkali hydrolysis as it is a less time consuming process [268]. However, bamboo fibre can also be extracted mechanically. Roller mill techniques (RMT) have been explored for mechanical

separation, as well as compression moulding treatment (CMT) [269].

To conclude this section, as described for retting, different extraction ways exist to obtain plant fibres. They strongly differ due to the plant structure, fibre accessibility and geographical culture and uses. Nevertheless, , the impacts on fibres can be strongly different according to the chosen extraction method. Modern scutching lines, potentially combined with hackling, enable to obtain high quality long fibres whereas aggressive extractions such as hammer mills generate damaged plant and fibres structures. In the following section we will focus on the impact of these extractions on fibre integrity.

2.5.3. Impact on fibre integrity

Elementary plant fibres may have numerous defects which can be from misorientations of cellulose fibrils (which may occur during the synthesis of cellulose and the formation of walls), some dislocations, sliding planes or knees [270]. These knees are the most visible defects by microscopy and are commonly referred to as kink bands. They are distributed heterogeneously over the length of the fibres, the mean length between two defects being about 100 µm ± 40 µm [271]; they may be revealed in polarised light. Their origin is not well known but it is probable that some of these defects are formed both during the bending of the fibres due to lodging but also during the phase of retting or drying of the fibres when the growth strains present *in-planta* are released. Thus, defects observed on the surface of flax fibres are found on non-scutched fibres and are likely to have developed during the growth of the plant [272]. There are also defects on the surface of hemp fibres from non-decorticated plants [273,274]. Hernandez-Estada et al. [275] demonstrated that decortication has the highest impact in inducing dislocations whereas coarse separation and carding has lower impact, but add more dislocation-like damage. Hänninen et al. [273] showed that following scutching and carding, the number of defects increases with respect to the hand-decorated fibres. In addition to the defects originally present in the fibres, the formation of kink bands may also occur during processing or extraction, particularly in the case of the scutching process [272] for flax. The defects (kink-

band, knees, dislocations) observable at the surface of the fibres are created during the transformation stages by bending and compression stresses and thus weaken the fibres, resulting in a reduction in their tensile strength (Andersons et al., 2009, Bos et al., 2006; Davies and Bruce, 1998). The development of defects on virgin fibres could be observed by studying the compressed face of the unit fibres of flax with the SEM during mechanical loop tests [278,279] or compression or bending [280] (Figure 23).

Figure 22

Thus, the mode of extraction of the fibres as well as the parameters of adjustment of the machines can have an influence on the quantity of defects created and thus indirectly on the performance of the fibres. Retting heterogeneities between different batches can also have effects on the performance of the fibres. Three major types of stress-strain behaviours were observed and described, mainly for hemp and flax [67,103], but in different proportions for each sample. The first one consists of a linear and truly elastic tensile behaviour (TI); the second one (TII) composes of two linear distinct sections with a decreasing slope in the second section, probably due to certain damage mecahnisms. The third one (TIII) displays a non-linear section at the beginning of the loading stage up to a threshold point, followed by a section where the tangent modulus increased up to failure. Aslan et al. [281] observed that the tensile response of a green (non-retted) flax was TI-type, as opposed to a retted, scutched and then refined flax with TI or TIII behavior. The authors explained the type TIII by the creation of defects due to mechanical treatments (scutching and refining). These results were confirmed by Lefeuvre et al. [60] 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 having been scutched at high speeds due to being under-retted. Apart from the scutching rate, which is dependent on the initial degree of retting of the plants, the various processing steps can influence the

performance of the fibres. Aslan et al. [281] compared the mechanical properties of elementary fibres from scutched linen and combing tow. They observed a significant drop in stress at break and Young's modulus of the fibres, which were 1445 ± 553 MPa versus 812 ± 342 MPa and 52 ± 16 GPa versus 30 ± 11 GPa, respectively. Moreover, the observed defects were more numerous for the fibres coming from combing tows. Thygesen et al. [282] compared the mechanical tensile properties of flax bundles after retting, scutching, carding, then refining. They observed a reduction in the strength at break of the bundles with the transformation steps. Depending on the protocol used (mechanical, manual, physical, physico-chemical, chemical, enzymatic) the impact on the cell walls will be different. Bos et al. [278] measured a lower average fracture stress for mechanically extracted fibres (1522 ± 400 MPa) compared to manually extracted fibres (1834 ± 900 MPa). Van de Velde and Baetens measured a rupture stress of 925 MPa for chemical fibres extracted chemically [283]. The fracture stress value is lower for chemical extraction; the reagents used during chemical extraction may have degraded the fibres decreasing their resistances. Bos et al. [278] showed that the breaking strength of hand-decorated unit fibres (1834 ± 900 MPa) was higher than that of scutched and combed fibres (1522 ± 400 MPa).

At the scale of the composite material, the amount of defects present also plays an important role in the performance of these materials. Le Duc et al. [284] demonstrated, by optical rheology experiments, that the fibres preferentially broke at the kink bands due to shear stress in the matrix. The number of kink bands, depending on the shear rates involved in the process, can thus have an impact on the fibre lengths in the composite thereby governing the fibre reinforcement capacity and the mechanical performance of the materials.

Figure 23

This has been demonstrated by Gourier et al. [285] who studied the relationship between the inter-defect distance and the final fibre length in a PA11-flax composite; They noted a strong

correlation between the inte-defect distance and the fibre length in the injection-moulded composite. The mechanical properties of the composites, and in particular their stress, are also influenced by the degree of individualisation of the reinforcements. By studying different fibre reinforced epoxy-flax UD composites with different degrees of retting, Coroller et al. [262] observed low fracture stresses for composites reinforced with under-retted fibres, due to the low degree of individualisation of the latter (Figure 23). Martin et al. [24] also found a greater division of the retted fibres, as well as better mechanical performance of injection-moulded composites compared to those reinforced by sub-retted fibres.

However, the impact of retting on the properties and performance of plant fibres has yet to be investigated. Indeed, the literature does not all agree. Van de Weyenberg et al. [286] measure mechanical properties of fibre bundles for green, half-retted and retted flax; the break stresses are 68.9, 72.8 and 71 cN.tex-1, showing no change in performance; the same trend was highlighted by Alix et al. [127]. On the other hand, Van de Velde and Baetens [24,283,287] (2001), Pillin et al. (2011) and Martin et al. demonstrated higher fracture stress and Young's modulus values for the most retted flax fibres.

Due to the enzymatic action, the retting leads to a modification of the biochemical composition of the plant. Meijer et al. [23] demonstrated the decrease in the amount of pectins contained in flax straw during retting. The proportion decreased from 3% to 1%. In addition, Rosemberg and De França [244] demonstrated the release of galacturonic acid during the retting with warm water of linseed stalks. The level of galacturonic acid increased during retting. The work of Pallesen [288] shows an increase in the proportion of cellulose in flax fibres with the degree of retting, from 70 to 76%. Akin et al. [239] showed that retting decreased the quantity of polysaccharides which is in agreement with the results of Pallesen, the ratio between cellulose and polysaccharides (rhamnose, arabinose, xylose, mannose and galactose) thus passing from 4.2:1 to 6.9:1. The phenolic proportions of compounds decreased until only traces were left. The phenolic compounds of un-retted fibres arises from residues of bark and xylem. Mooney et al. [289] also highlighted a significant change of the composition of pectic and hemicellulosic polymers. The retted fibres had a smaller proportion of rhamnogalacturonan (pectin), arabinane

and xylan (hemicelluloses). The total loss of polysaccharide caused by retting is estimated to be more than 3%. In the study by Akin et al. and Mooney et al., the proportion of glucose is not decreased, suggesting that retting did not attack cellulose fibres.

In the literature, an increase in the crystallinity of plant fibres during retting was obtained by X-ray diffraction crystallinity index measurements [290]. Zafeiropoulos et al. [291] report an evolution of 64.55% to 71.64% of the crystallinity index between green and dew retted flax. Li et al. (2009) studied the evolution of the crystallinity index between green and retted hemp fibres, after one and two weeks in moist atmosphere in hermetic bags. The crystallinity index evolved respectively from 66% for green hemp to 85% for red hemp. Finally, Marrot [292] reports an increase in the degree of crystallinity of hemp fibres following the retting in the field of the plant. The crystallinity index increased by 45.8% for green hemp, to 71.3%, 71.2% and 74.5% respectively after 14, 31 and 45 days of ground retting. Interestingly, in case of over-retting, a decrease in the degree of cristallinity is observed for hemp fibres, due to enzymatic alteration of cellulose in case of prolonged field stay [249]. These various works highlight the influence of extraction processes, but also of retting on the quality of plant fibres and their mechanical properties. The choice of the extraction process parameters is therefore extremely important to produce high-performance fibres; it will consequently also condition the properties of the composites.

2.5.4. Environmental aspect

Eco-design, validated by standard tools such as Life Cycle Analysis (LCA), allows environmental parameters to be integrated from the design to the end of life stage of products. It enables to precisely quantify environmental impacts. This further enables alternative materials to be compared with existing solutions under rigorous conditions as well as to design and propose diversified scenery in order to improve the product life cycle.

Regarding plant fibre production, several factors may affect the amount of fossil energy sources replaced or conserved, such as the cultivation parameters and biomass yield. These

parameters can be highly dependent on geographical location and climatic conditions. In this way, water need is a crucial parameter for the environmental assessment of fibre production. Correia et al. [293] showed that, in the case of manufacturing of kenaf insulation panels, the irrigation step was one of the key factors contributing to energy consumption. Through a sensitivity analysis, they showed that lowering the level of irrigation increases the energy efficiency, despite the reduction in yields . Moreover, delaying the harvest from October to December increases the energy efficiency due to more favorable hydric conditions. The dependence on water of plants is not the same for all the species. Fernando et al. [294] calculated the deficit between available water and the water requirements of different crops grown in the Mediterranean basin. They showed that this deficit was 117 mm per year for kenaf whereas it is very high for hemp (467 mm/year) and only 31 mm/year for flax. Thus, specific species such as kenaf are described as opportunistic in relation to water availability, with a high rate of stomatal conductance and transpiration rate when water is not limited, and a markedly reduced stomatal conductance and transpiration rate when water availability is restricted [295]. Investigations on textile flax fibre showed that, despite a severe drought, mechanical properties of elementary fibres were unchanged [60]. According to the plant species, the water consumption during growth can be strongly different. Thus, cultivation of kenaf needs around 450 mm [296] of water whereas this quantity is 800-1000 mm for cotton [297], 150-250 mm for flax [200] or 2000 mm for curaua fibres [298]. In case of flax, hemp or curaua, fields don't need irrigation, the annual precipitation being sufficient. Things are different for kenaf [296] and cotton, however. About 53% of the global cotton area is irrigated and mainly located in dry regions: Egypt, Uzbekistan and the province Xinjiang of China are entirely irrigated, whereas in Pakistan and the North of India irrigation supplies most of crop water. Consequently, in Pakistan already 31% of all irrigation water is drawn from ground water and in China the extensive freshwater use has caused falling water tables. Thus, due to this over-consumption of water, the cultivation of cotton has led to ecological disasters such as the disappearance of the Aral Sea and the Chad Lake. To produce 1 kg of cotton fibres, 7,000-29,000 liters of water are required [297], in contrast to only 600-1000 liters being needed for 1 kg of scutched flax fibres [200,299]. Moreover for flax, this water is provided entirely by rainfall, showing the importance of choosing

the culture from one region to another, taking into account both local climate and plant needs. Experimental flax cultures have been conducted in arid regions of Spain [300]; their environmental analysis shows that 71% of their energy needs have been used for irrigation, whereas it is non-existent in the treadish-growing regions located in France or Belgium.

In addition, pesticide use is an important contributor to environmental impacts. The share of cotton on global pesticide sales has averaged 11% and on the global insecticides market around 24% [297]. At the same time, cotton acreage amounts to only 2.4% of the world's arable land. Thus, it is obvious that the pesticide use for cotton in relation to the area is disproportional. Conversely, kenaf or flax present low pesticide impact, reflecting their low susceptibility to pests and diseases. The pesticide score associated with the production of kenaf [296] is comparable to the score reported for flax [301] but higher than what is reported for hemp [294] or jute [14]. Mainly due to pesticide and water consumption, strong differences can exist between LCA; as an example, primary energy inputs for the production of 1 ton of hemp and cotton fibre is 8.2 GJ and 25.2 GJ, respectively [302].

Yields can also affect the energy efficiency and the energy balances [293]. The higher the yield of the crop, the higher tends to be the energy efficiency of the system and the amount of fossil energy saved. The average yield of cotton is 854 kg per hectare for irrigated cotton and 391 kg per hectare for rain-fed cotton [297]. These yields are strongly lower than flax or hemp ones, especially regarding the water consumption. For hemp, yield can be influenced by the cultivation method; according to Van Der Werff et al. [303], scutched fibre yield for water retted and baby hemps, is 2073 and 1041 kg/ha, respectively. In case of flax, Bourmaud et al. [59] indicated a total average fibre yield of 2059 ± 941 kg/ha on 11 batches of Marylin textile flax, cultivated for consecutive 4 years. This fibre yield is highly dependent on the extraction method and sometimes difficult to compare between plants. In case of jute, kenaf, hemp and flax, fibre yield is 5% [304], 30% [296], 33% [305] and 36% [59] of the total biomass, respectively, whereas it is around 70% [306] for China reed; but it is not possible to compare the quality of extracted long fibres with milled biomass such as bamboo or reed. The grinding of China reed represents only 3.3% of the total energy consumed for fibre production, in case of flax or hemp,

the scutching step is the main contributor [300].

After the cultivation step, the extraction phase could be considered as being the main environmental contributor for fibre production, even if this assessment were moderated according to fibre variety. In a general way, Van Dam et Bos. [307] claimed that natural fibre production requires less than 10 % of the energy used for production of PP fibres (ca 90 GJ/ton) and ca 15 % when the use of fertiliser was included. Rettenmaier et al. [308] and Pervaiz and Sain [309] also reported that biomaterials from fibre crops (e.g., hemp and flax) are superior to their fossil or conventional equivalents in terms of energy savings ; a 60 % net energy savings was stated by using 65 % natural fibres (hemp) instead of 30 % glass fibres in thermoplastic matrix. Moreover, Joshi et al. [310] compared the non-renewable energy requirements for the production of composite reinforcement; they obtained 54.7 MJ/Kg and 9.55 MJ/Kg for glass and flax mat, respectively.

Figure 24

Le Duigou et al. [301] explored the environmental impacts of flax fibre production compared to glass ones. A significant reduction of abiotic depletion (-90%), human toxicity (-98%) and photochemical oxidation (-88%) were underlined. Nevertheless a higher eutrophication (+17%) was noticed for flax due to the use of fertiliser or pesticide during the growing phase. The mechanical treatments have a strong impact on environmental assessment; for flax, they represent 35% of the non-renewable energy consumption and they are highly increased in the case of hackling. The energy consumption by scutching is 4.4 MJ/kg of fibre whereas it is 11.6 MJ for hackled fibres; but this data must be viewed in comparison to that of other fibres. Indeed, for 1 kg of cotton yarn, Blackburn et al. [311] calculated an energy consumption of 33.1 MJ. Mechanical treatments can have various impacts according the plant; for jute and kenaf fibres, carding energy represents 0.13 KWh [14] and 0.20 KWh [296] for 1 kg of fibres, respectively. The LCA can also be impacted by the way of retting; Van der Werf et al. [303] compared

cultivation of hemp and flax by using 3 different scenarios for hemp (water retting, bio retting and baby hemp cultivation) and conventional cultivation for flax (dew retting). A higher pesticide use was underlined for flax as well as a strong water use during processing for hemps water and bio retting. Bio-retting had higher impacts than the reference scenario for climate change and energy use, due to higher energy input in fibre processing. Baby hemp exhibits higher impacts than the reference scenario for eutrophication, land occupation and pesticide use. A reduction of the environmental impacts of hemp yarn should give priority to reduction of energy use in the fibre processing and yarn production stages and to reduction of eutrophication in the crop production phase.

3. Diversity in views on plant cell walls

In this section, we will discuss the fundamental understanding of vegetable fibres from a biologist's and an engineer's perspective, and also compare experimental methods and tools both employ fibre. Indeed, the perspectives of these two communities are very different, even opposed sometimes, which can lead to interesting conceptualisation of problems. We will then explore discrepancies due to methods of experimental characterisation, including those arising from scale problems (e.g. modulus measurement at cell wall, fibre or bundle scale), and compare what mechanical or biochemical behaviours can be measured through the different methods. The final discussion will look to address the question: which plant fibres are relevant for high-performance composite materials?

3.1. Biological approach

      3.1.1. Classification based on location in–planta and cell growth behaviour

The biologist's view reveals major differences between the location, the formation and growth of different plant fibres. Their view is intimately linked to the location of the fibres in the plant among the different tissues and their functions in the plant. A number of classification

approaches have been proposed. Van Dam and Gorshkova [159] propose to classify vegetal fibres according to whether they exist within or outside the xylem. Xylem fibres would include tracheids and libriform fibres, as well as gelatinous fibres present in tension woods. Fibres outside the xylem are typically those present in the cortex, in the phloem, or located on the periphery of vascular tissue. Mikshina et al. [146] propose a similar classification which divides the plant walls into two large families, those consisting predominantly of xylan, or those that are gelatinous. This distinction is a priori simplistic but makes it possible to distinguish, in a pertinent way, the functions of the fibres within the plants but also to make the link between the biochemical features of the walls and their mechanical performances. We have already discussed this point in detail in Sections 2.2.1. and 2.4.2. Another possible classification is to distinguish between monocotyledons and dicotyledons within angiosperms [312]; however, this classification does not allow the fineness of the previous one, as monocotyledon supply fibres mainly located in the leaves (sisal or abaca) or in the palms. Finally, in agreement with Van Dam and Gorshkova [159], it is also possible to classify the fibres according to the type of meristem that produces them. The primary fibres (those of flax, for example) are formed by the primary meristem located at the apex of the plant whereas the secondary networks appear when the plant has reached its maximum height during a secondary growth coming from a tangential division of the cambium cells. These secondary fibres are rather localised at the bottom of the stem and can be found, for example, in hemp.

Figure 25

Figure 25 is an illustration of a synthesis of this discussion and presents the main varieties of plant fibres according to their location within plant tissues. The function of its tissues differs, some ensure, for example, a role of conduction of the raw or elaborated sap, others are constituted only by fibres intended to support the plant and ensure its stability. The fibres found

there exhibit, as we have already explained, different functions and geometries, but also very diversified modes of growth.

In the case of flax, fibre growth is well-described in literature. Throughout the growth of the plant, fibres are formed in a coordinated manner with the criblo-vascular bundles (conducting tissues) of the stem; this occurs in four distinct steps: 1) fibre cell multiplication at the top of the stem [317], 2) cell elongation in the top 3-5 cm segment of the stem top, 3) fibre radial expansion and thickening of the walls below the snap point, a zone defined in [318] where the stiffness of the stem increases significantly, and 4) structuring of the wall leading in some cases to a reduction in the cell wall thickness and consequently fibre diameter [319,320]. The latter occurs after seed formation, in certain varieties and/or as a function of the environment.

During the second phase of elongation, which lasts 3 to 5 days per fibre [64], the cell extends by around 5 to 20 mm per day [167] to reach up to 100 mm [194] mainly by so-called intrusive growth. This enables the fibres to penetrate through the shared lamellae between neighboring cells [167]. If intrusive elongation starts with tip growth leading to a spindle-like shape of the fibre, the main part of elongation occurs by diffuse symplasmic growth along the entire cell [320,64,167]. This means that the final length of the cells is obtained not by classical division (multiplication of the chromosomes and cellular division cellulaire by construction of a septum then laying down a cell wall on either side of the septum) but uniquely by multiplication of the nuclei and then by cellular elongation. At the end, each fibre can possess several tens of nuclei [167].

This extension of the fibres stops progressively at the snap point [194]. The fibre is then, as all cells, bounded along its whole length by a continuous primary cell wall, whose cellulose mesofibrils are aligned parallel to the growth direction. The thickness of primary wall is between 200 and 500 nm [321] and it is usually made up of one third pectins, one third hemicelluloses (see the definition below) and one third cellulose [322]. The third phase corresponds to the synthesis of a secondary cell wall which, little by little and layer by layer, is filled with cellulosic fibrils.

This intrusive growth takes place in a similar way for the other main primary fibres from the phloem, namely hemp and nettle. In the case of these fibres, the elongation phase (step 2) propagates across the top of the stem within the tissues being in a structuring process and this intrusive growth makes it possible to obtain long fibres. For example, ramie fibres can reach lengths of around 550 mm [323] and extend almost along the full length of the stem. Those of flax have average lengths between 20 and 40 mm [159,166,324] and hemp fibres are generally shorter with lengths of about 15 mm [167]. The origin of the differences in lengths between fibres at the end of the elongation is still unknown. However, it may be related to the ability of cells to produce several nuclei. Flax fibres have the peculiarity of presenting multiple nuclei distributed regularly along the fibre length. In both flax and hemp, there are on average 80 and 50 [64] in the same cell. In the case of wooden tracheid cells, the number of nuclei is generally 5 for a length of about 1 mm [325]. Therefore, a high number of nuclei may be considered as a prerequisite for significant elongation. However, we do note that the seminal hairs of cotton, although reaching lengths of several centimetres, possess only one nucleus [159]. For the majority of plant fibres, this division of the nucleus begins in the differentiation step at which two nuclei are present.

For secondary fibres originating from the vascular cambium such as hemp, their growth mode is also intrusive. Their population is regulated by the activity of cambium during secondary growth. The development of these mononuclear fibres [64] is carried out in already formed and structured tissues, their growth beginning at about 600 or 700 mm from the apex in hemp, whereas that of the primary fibres begins to a few tenths of mm of the latter [326]. Thus, their growth can only be carried out intrusively without a symplastic phase. This is demonstrated by their length which is greater than that of the surrounding cambium cells and by their tapered tips [324]. However, their growth is reduced and they do not exceed a few millimetres [327]; this is the case for secondary fibres of hemp, jute and kenaf. One possible explanation for the large variations in fibre geometries within a plant might be that both primary and secondary phloem fibres are pooled [78]. For instance, in jute the outer primary phloem fibres are ~3.2 mm long, whereas the inner secondary phloem fibres are only ~1.5 mm long [328]. The differences in length between primary and secondary bast fibres are even more pronounced in hemp, where

primary fibres reach lengths of up to ~25 mm and secondary fibres reach lengths of only up to ~2 mm [329]. Whether for very short fibres (having lengths typically under 1 mm when coming from xylem), fibres a few milimeters in length from the secondary phloem, or long fibres of the primary phloem, intrusive growth mode is favoured and confirmed by the predominantly tapered shape of the mature fibres [324,327]. This is also the case for the fibres located in the conductive bundles of leaves [330].

Finally, for the biologist, specific terminology also makes it possible to consider the fibres according to their strict definitions, based on their shape, length and mechanical function in the plant, for example [159,63]. If the word fibre is sometimes overused for sclerenchyma cells or for vascular cambium elements, it is even more obvious for cotton trichomes or kapok testa trichomes. The latter elements do not originate from the sclerenchyma but constitute growths of the seeds produced on the surface of the ova at the time of flowering [159]. They show considerable elongation by diffuse growth of several centimeters while being mononuclear. Cellulose filling of the trichomes begins 15 to 20 days after flowering. The process has several sequences for biosynthesis, with layers being produced having alternate MFAs.

3.1.2. Are the S2-layer structural models universal?

All fibres from the plants in Figure 27 have a secondary cell wall within which the S2-layer dominates. However, we have discussed in Section 2.4 that the geometries of this S2-layer differ greatly according to the plant species, and sometimes even within the same specie. Significant differences in the structure and parietal composition of S2 also exist. Thus, the S2-layer cannot be considered equivalent for all plant fibres.

As mentioned above, the parietal biochemical structure of the plant fibres can be differentiated according to the plants under consideration. In agreement with Van Dam and Gorshkova [159] and Chernova and Gorshkova [327], fibres derived from plants can be classified into two broad categories from a biochemical and structural point-of-view (Section 2.2.1). The first group is the xylan-type and is the more common. It concerns different types of wood cells but is also found in fibres derived from stems such as jute and kenaf. These walls are characterised by a high MFA, by small thicknesses of secondary walls (generally between 1 and 4 µm), but also by high

levels of lignin and xylan. Gelatinous fibres form the second group. They possess matrix polymers rich in galactose and high cellulose contents of up to 85% [331]. Unlike xylan fibres, these walls possess small MFAs as well as high wall thicknesses, generally between 10 and 15 □m thick. These fibres are mainly derived from flax, hemp or even ramie phloem but can also be found in bamboo (we will return to this plant later in this section). They have very low levels of lignin, and the lignification occurs only after the filling and structuring of the S2 walls, that is to say at the end of the plant life [327]. This is not the case for the xylan-type walls for which lignin deposition takes place during the filling of the walls. We therefore deal with two types of cell walls, both constituting the S2-layer but with major differences in structure and properties. This gelatinous layer (often referred to as the G-layer in literature) is present in the fibre plants mentioned above but it is also found in some cases in wood. Indeed, particular structures named 'reaction' wood are generated when branches, for instances, must reorient in the presence of external forces and stimuli. This reaction wood is defined as 'compression wood' for gymnosperms as compressive stresses are induced in the lower part of the branches, whereas the term 'tension wood' as used for the reaction wood of angiosperms as tensile stresses are generated on the upper part of the branches [332].

Angiosperm tension wood includes this so-called G-layer which is produced to restore the tree verticality in case of tilt or permanent loads [156,333]; it is positioned on the upper side of the bent part of the branch or trunk [334]. According to Chernova et al. [327], G-layer is formed upon shoot bending. Its genesis is due to gravitational and/or mechanical stimuli. The more the shoot or branch is bent, the more tension wood develops in it [335]. Tension wood formation is governed by two main phenomena: the triggering of cambial activity, expressed by an increased number of cambial cells and eccentric wood increment [336], and induction of G-layer in the fibres. The preponderant role of auxin has been showed in the formation of the G-layer, with differences (deficit) in auxin distribution due to plant inclination being a triggering factor of G-layer initiation [327,335]. In tension wood, the gelatinous layer can replace the S2 and S3 layers in the secondary cell wall, or be an additional layer [156]. This gelatinous layer is generally more thicker than xylan-layer, being up to 15 μm thick [331]. The G-layer can occur in wood but also in plant fibre secondary cell walls such as hemp or flax. In such plant phloem fibres, the S2-

layer is completely composed of the G-layer. Nevertheless, a thin xylan layer remains at the periphery of the S2-layer, evidenced thanks to the use of the LM11 antibody on phloem flax fibres [337].

Thus, the common presence of this G-layer shows that the secondary wall of tension wood is probably closer in its structure and composition to a flax cell wall than to an S2-layer of normal wood. Nevertheless, major structural differences exist especially in terms of the degree of development of the initial S2-layer, as mentioned above, it is very reduced in flax whereas it still occupies a significant place in wood. The secondary wall of tension wood is thus composed of two radically different layers in terms of biochemical composition and MFA, a true composite, while that of flax is a more homogeneous material in comparison. Figure 28 provides a summary of these differences.

Figure 26

As explained by Gorshkova et al. [338], the difference in xylan layer thickness between wood and flax can be attributed to specific needs in radial compression resistance. In annual plants, the mechanical forces acting on developing phloem fibres in the radial direction may be weaker than in woody plants, inducing a xylan layer with reduced thickness.

The formation of G-layer during plant growth is progressive and can be clearly distinguished on immature plants. On flax and hemp fibres, Gorshkova et al. [331,232] evidenced the coexistence of two layers on secondary cell wall of growing plants. The initially deposited layer is called Gn and progressively, this Gn-layer is converted into G-layer in the outer area; indeed, the thickness of outer the G-layer gradually increases until the total disappearance of the Gn-layer. The transition from Gn to G layer is coupled with increase in cellulose crystallisation [334] and an important change in layer structuration, mainly induced by galactan positioning. In the newly deposited Gn-layer, galactan is not tightly bound within cellulose microfibrils, whereas in the G-layer cellulose microfibrils lock matrix galactans, to form so-called entrapped galactans (Fig. 26) [331,339]. This results in tension, giving rise to specific mechanical properties of

gelatinous fibres, in particular contractile properties making possible an analogy between plant G-layer and muscles [340,341]. Thus, Gn-layer evolves towards a more homogenous and compact structure; the new G-layer also exhibits a lower MFA, with the galactans being responsible for the cellulose fibril reorientation [331]. Mechanically speaking, Arnould et al. [342] underlined these structural differences by highlighting a stiffness gradient between the Gn and G-layers through Peak Force Quantitative Nano Mechanics (PF-QNM) measurements.

As described previously, despite the existence of two main types of cell wall layers (gelatinous and xylan), several authors agree that the S2-layer is homogeneous in terms of structure, but nuances may appear at the level of the boundaries with the other layers. As explained previously, plant fibre G-layer can exhibit a thick xylan layer at the S1-S2 interphase. In the same way, Roland et al. [343] proved, thanks to Transmission Electronic Microscopy (TEM) analysis, progressive changes in MFA in this area. Thus, most bast and wood fibres exhibit a quasi-homogenous S2 layer.

Nevertheless, some nuances exist especially for plants with slow (compare to annual plants such as jute, hemp or flax) growth such as bamboo. Indeed, in case of monocotyledonous plants such as bamboo (Fig. 15), fibres stay alive during the whole life of the plant [344] and successive secondary cell walls with different MFA are deposited during ageing. Thus, bamboo S2-layer can be assimilated to a multi thin-layer structure. Moreover, Liese and Parameswaran [345,202] evidenced that thick and thin layers alternate. In the same way, cotton trichomes also exhibit a specific structure; the secondary cell wall is made of concentric layers of pure cellulose with a significant evolution of the MFA through the fibre diameter. Close to the primary wall, MFA is around 45° and becomes aligned more closely with the fibrillar axis as lumen is approached [346]. Moreover, the direction of MFA twist changes at frequent intervals along the fibres [347] by following an arc; indeed, when a set of spiral cellulose strands ends, a new set of spiral strands starts growing in the opposite direction. Furthermore, the daily cycling of temperatures during secondary cell wall formation may generate layering in the fibre wall inducing a multi-lamellar structure, growth being diurnal [347,348].

3.2. Mechanical approach and identifying the pertinent scale?

The characterisation of plant fibres can be carried out at different scales: bundles, elementary

fibres or plant walls and layers. In polymer composites reinforced by plant fibres, these various

elements are generally present. The presence of elementary fibres or bundles depends on the

degree of refining of the fibres and in particular on the extraction conditions, so that the

scutched fibres will generally consist of bundles of fibres, whereas if they have undergone in

addition a combing step, their individualisation will be more pronounced and some lots may

comprise a majority of elementary fibres [44]. The degree of retting may also play a major role in

the ease of extraction of plant fibres, and the degree of alteration of the adjacent lamellae will

play a major role in the nature of the fibrous objects present in the final composite. Finally,

depending on the nature of the plants and the morphology of the stems and fibres, we are

dealing in some cases with highly cohesive fibre bundles. In this case, the associated

composites essentially comprise bundles, for example, jute [46]. Thus the different scales of

characterisation can give pertinent and complementary information. In this section, we propose

to detail the different approaches in order to compare the information obtained and to discuss

their relevance. Four scales of measurements will be detailed here: from the stem to the plant

wall. Figure 27 details our approach.

Figure 27

3.2.1. Mechanical characterisation of plant stems

This scale is not the most widespread but it provides important information on the relationship

between stem structure and plant stability. Plant buckling risk is an important biomechanical

characteristic of plant growth strategy and can be easily estimated by knowing morphology and

weight of stems. Thus, the Greenhill model [349] is widely used to estimate the lodging risk by

comparison between the plant height and the critical buckling height [350]. The stem mechanical informations can also indirectly provide suitable details about cell wall stiffness as well as fibre contribution in plant stability. For example, Chandio et al. [351] explored the bending strength and Young's modulus of both wheat and rice straw; they evidenced high stiffness for wheat as well as Young's modulus differences according to the internode's position; the obtained conclusions were helpful to design straw equipment, especially harvesting machines and scutching implements.

Mechanical testing can also be performed in order to estimate and quantify the lodging risk of crops. Indeed, a vertical stem can buckle as an entire unit due to its own weight or due to an additional load imposed from fruit, leave, flower, branch or exogenous parameters such as rain or wind. Schulgasser and Witztum showed that [352] the high degree of anisotropy present in tubular plant stem is a dominant factor for failure mechanisms. Along the same line, Leblicq et al. compared the phenomenon of ovalisation during bending on PVC tube [353] and wheat and barley stems. They found analogies between the two materials with a specific behaviour including a first ovalisation phase then a buckling phase; after pronounced deformation, resistance to bending and consequently lodging of crop stem was greatly reduced. The authors compared the bending behaviour of wheat and barley and evidenced correlations between the crop species, growing conditions, stem diameter, cell wall thickness and bending behaviour. Interestingly, they demonstrated that bending tests can be used to estimate the cell wall thickness and that a core ring structure, with a cellular core of lower density than the outer shell, can significantly increase the bending resistance of plant stems. Similar conclusions were obtained by Deger et al. thanks to numerical modelling [354]. These kinds of structures are similar to the structure of a flax stem and offer explanation for the extraordinary length to diameter ratio of this plant (Figure 12). Methodology of bending tests on plant stems is important and sample precautions must be taken to avoid any errors in strength measurement [267]. Robertson et al. [355] performed bending tests on bamboo, giant reed and maize stems. They showed that internodal-loaded three-point bending test can produce erroneous measurements by inducing a early breakage of the plant and that maximising the span length and placing the loading point at stronger and denser nodal tissues give more reliable results.

Specifically on flax, Bourmaud et al. [59,22,356] performed bending tests on flax stems in order to quantify the lodging stability of flax (Figure 28).

Figure 28

These works provide an original method to determine the stiffness of dried or green fibres contained inside the plant. Four flax varieties (Marylin, Aramis, Eden TDL21, Telios and TDL25) with distinguished lodging resistance were studied. After mechanical characterisation of elementary fibres and morphological analysis of stems, we showed, by flexural tests on green and dried stems, that it was possible to correlate the stiffness of the stems with the Young modulus of the elementary fibres, as well as their internal organisation. This result confirmed the crucial role of fibres in the support of the plant, and in particular on lodging behaviour.

Thus, mechanical testing on plant stems can provide specific information on plant structure and lodging stability. Interestingly, they also enable to estimate elementary fibres stiffness by an inverse method, based on known fibre volume fraction in a stem cross section obtained from architecture and morphology analysis.

3.2.2. Mechanical characterisation of plant fibre bundles

Elementary fibre properties have been evaluated extensively.Hhowever, most plant fibre-reinforced composites consist of plant fibres in the form of bundles and it is close to impossible to perform tensile tests on elementary fibres with conventional equipments for some plant varieties having short fibres such as jute, kenaf, sisal or abaca. Some researchers have developed tensile tests on fibre bundles in order to estimate elementary fibre properties. Even if bundle tensile properties are not representative of the intrinsic elementary fibre mechanical behaviour, they allow obtaining pertinent information in terms of stiffness or strength.

Plant fibre bundles are mainly composed of elementary fibres but depending on their retting step or the plant microstructure, they may contain a significant proportion of middle lamellas. Thus their tensile properties are governed both by the individual elementary fibres and the middle lamella. Bundle characterisation is widely used in industry after fibre extraction and scutching to select and qualify for some intermediate products, such as yarns for textile applications. The general behaviour of plant fibre bundles is described by different authors [357–360]. Thus Xue et al. [361] investigated the effects of temperature and strain rate on kenaf fibre bundle tensile properties. They observed a large scattering in mechanical properties and a strong dependence of tensile strength on the strain rate. Romhany et al. [357] explored the tensile behaviour of flax bundles, and noticed three distinct steps in their failure sequence, with firstly longitudinal splitting along the boundaries of the elementary fibres, then transverse cracking of the elementary fibres, and finally a fracture of elementary fibres and their microfibrils. By coupling an acoustic emission device to the tensile system, Barbulée et al. [360] were able to identify the different mechanisms of rupture of a bundle when subjected to uniaxial stress. It is thus possible to identify phenomena of friction between the non-joining fibres, breaks in the elementary fibres, delamination within the bundle as well as abrupt and sudden breaks within this bundle. The accurate measurement of the fibre cross-section (i.e. diameter) is a key point for accurate calculation of fibre tensile properties. Haag and Mussig [358] studied the scatter in tensile properties of flax bundles by using several specific methods to determine the bundle diameter. They showed that the main difficulty is to correctly estimate the cross-sectional area. Thus, they found tensile strength from 470 ± 147 MPa to 1465 ± 638 MPa on the same fibre batch according to the measurement method. Nitta et al. [362] validated a new cross-sectional area estimation method; fibre cross-section was changed from a polygon shape to an elliptical one and then the areas were correlated with hexagon-approximated cross-sectional area, which was calculated by measuring the projection widths on the fibre along 0°, 60° and 120° directions.

Interestingly, bundle tensile tests can also provide pertinent informations on middle lamellas, located between the bundle elementary fibres and mainly made of pectic polysaccharides or calcium pectates [363]. Charlet and Beakou [364] have shown that by increasing the specimen

gauge length, the tensile strength decreases, highlighting thus the involvement of the middle lamellae in the bundle strength. Conversely, by decreasing this distance (below 10 mm), fewer middle lamellae will be involved and the obtained strength is more representative of an elementary fibre. Thus, due to the length of the elementary fibres, these tensile tests on bundles are highly dependent of the gauge length, especially for long fibres such as hemp, ramie or flax. For example, for flax fibre bundles, Romhany et al. [357] calculated a strength at break of 613 MPa, 454 MPa and 264 MPa for gauge lengths of 20 mm, 40 mm and 80 mm, respectively.

In the same approach and by performing tensile tests on beams containing only two elementary fibres, Charlet and Beakou [365] were able to estimate the shearing of the interface between the two fibres. This value was about seven times lower than the one usually measured between a flax fibre and a petro-sourced thermoplastic matrix [366]. It is therefore conceivable that for materials reinforced with low divided plant fibres bundles, the rupture will be more easily produced within a bundle than at the interface between the bundle and the matrix; thus these bundles can be assimilated to weakness areas as it was already evidenced at the composite scale [367]. It is therefore important to prioritise the work of fibre cleaning and division occurring during the scutching step, to obtain fibre reinforcements as individualised as possible. Even if the fibres are assembled in bundles, the level of resistance of these objects within the composite can be good; indeed, the resin can diffuse between the fibres and strongly reinforce the interfaces. This local impregnation is strongly linked to the degree of retting and scutching of the technical fibres. For bundles with low tensile strength, the breakage is mainly monitored by the interface's quality [368].

Of course, the bundle division and morphology is directly linked with the level of retting of the plant fibre batch. Thus, bundle characterisation is an indirect way to estimate the degree of retting. In a batch, fibres are never fully individualised [262] and the middle lamellae properties are dependant on the retting quality and homogeneity; if the retting is generally homogenous for flax due to a long cultivation history, it can be different for other species. For example, in the case of hemp, dew retting is less controlled and stems are stacked as large piles inducing heterogenous retting fully dependant on the accessibility to micro-organisms, water or sunshine.

Liu et al. [369] performed tensile tests on hemp strips at different stages along the retting process; they evidenced a progressive decrease in tensile strength, attributed to both cellulose and middle lamellae degradation. Liu's hypothesis on cellulose degradation was recently confirmed by Placet et al. [249], where the crystallinity index of over-retted hemp fibre was found to be significantly lower compared to non-retted fibre.

To conclude this section, an interesting piece of work dedicated to the understanding of biocomposite fracture behaviour was published by Hbib et al. [370]. The authors performed transverse tensile tests on a polymer-elementary hemp bundle system. Localised damage within the bundle was highlighted in the elasticity stage. Another work investigates crack propagation (2–149 m/s) until rupture in both elementary fibre and bundles using laser generated defects within fibres, coupled to a high-speed camera. Experimental investigations in combination with finite element simulations show that the damage kinetics are a combination of growth and coalescence of micro-cracks, and failure is achieved by crack growth in the transverse direction but is limited by the coalescence of micro-cracks in the longitudinal direction. The effect of defect geometry appears to be of interest for fibre mechanical processing optimisation [371]. These different examples show the need and interest in performing mechanical tests on plant fibre bundles, not only to determine fibre properties, but also to understand the behaviour of the middle lamella, and consequently the degree of processes such as retting, or to better understand damage mechanisms within biocomposites.

3.2.3. Mechanical characterisation of elementary plant fibres

Tensile characterisation of elementary plant fibres is possible with conventional equipments but restricted to long fibres such as flax, ramie or primary hemp fibres. When fibre length is too short, handling and use of a tensile testing machine become complex; the acceptable minimal length can be defined as ~ 5-15 mm length. For short fibres such as those of wood, specific protocols have been developed. The first published protocol was by Jayne [372], who used a conventional tensile testing machine, but clamped the fibre ends using abrasive paper. The method was modified by Page [373] by using glass tabs at the end of wood pulp fibres, and

further optimised by Burgert et al. who used paper frames to mount the wood fibres, with this method being widely used for both short and long plant fibres due to its easiness in handling. Kersavage [113] developed a slightly different protocol based on the use of epoxy droplets at the ends of the fibres in order to minimise stress concentrations close to the gripping of the fibre ends. Groom et al. [114] improved Kersavage's method. Recently, Wang et al. [108] performed tensile experiments by using the epoxy droplet method on elementary bamboo and kenaf fibres. Ren et al. [48] and Yu et al. [49] tested several tens of bamboo fibres of different ages with the same method. These methods were developed more than 50 years ago but they are not widely used due to the difficulty in handling short elementary short fibres. Whatever the used protocol, elementary fibre tensile testing cannot be performed for fibres shorter than 5-7 mm [221]. Moreover the extraction of short fibres is not a trivial process and can induce bias due to damage to the fibre integrity through any mechanical or chemical treatment used in the extraction process. However, as we will discuss in the next section, other forms of short fibre mechanical testing can be performed by nanoindentation without fibre length limitation.

For long plant fibres such as hemp, ramie or flax, tensile characterisation is easier. These tests are generally performed by using a paper frame, with the elementary fibres being glued with epoxy resins on the frame; the system is then put on the tensile machine and the frame edges cut before loading. The experimental conditions as well as the tensile properties calculations are detailed in the XPT-25 501-2 standard [374] dedicated to flax elementary fibres characterisation. This standard represents an important advance in terms of uniformity of the tests, but some points can still be improved upon: i) the determination of the useful cross-sectional area (CSA) (see 3.3.4. section) remains difficult and recent work has highlighted the important impact of the measurement method [358], ii) the determination of the overall deformation (i.e. strain) also remains an important source of uncertainty, iii) the relevance of determining the elastic modulus before or after expression of any non-linear behaviours, and iv) the boundary conditions may vary according to the nature of the glue used, the thickness of its deposit, the twisting of certain fibres or the hygro-thermo-mechanical loading.

Altogether, a plant fibre can be described as a complex composite multi-layer structure. Its respons to tensile stress are governed by interactions and interfaces between the cell wall layers. Consequently, the stress–strain curves of cellulosic fibres are not expected to be simple [149]. The stress–strain curves of cellulosic fibres including flax [149,375–377] and hemp [67,378,379] have been found to be quite complex by being nearly elastic or displaying distinct non-linear regions. In the case of hemp, cellulosic fibres have been reported to display three types of tensile behaviour in response to tensile testing [67,378,380] (Figure 29.a). Same behaviour has been showed on elementary flax fibres [103] (Figure 29.b). Type I (TI) exhibited a linear relationship similar to that observed for glass fibres. Type II (TII) was non-linear and characterised by two distinct sections with a decreasing slope in the second section. Type III (TIII) has been reported in the literature as being the typical behaviour for an elementary flax fibre [149].

Figure 29

This third type TIII showed non-linearities with a stiffening effect after a threshold point due to microfibril reorientation during tensile loading [103] (Fig. 29.c). In the first part of the curve, the value of the tangent modulus (designated as E_{T3} for type III behaviour) was observed to decrease down to a minimum (named $E1_{T3}$) within a strain range between 0.2% and 1.3%. Then, E_{T3} increased up to a plateau before rupture (named Er_{T3}). From this particular variation of E_{T3}, two deformation domains were defined (Fig. 29.c); the former, going from zero to $\varepsilon1_{T3}$, covered the non-linear behaviour; the latter, $\varepsilon2_{T3}$, corresponded to the part where E_{T3} increased. Additionally, εr_{T3} was the total deformation at the sample rupture. Lefeuvre et al. [103] studied these specific behaviours and compared several flax batches over 3 different cultivation years; they linked mechanical behaviour and biochemical properties. They suggested that structuring polysaccharides, having links between cellulose microfibrils, were more related to the first non-linear section of the stress–strain curve whereas the matrix polysaccharides, in which cellulose microfibrils are embedded, could influence the second section of the stress–

strain curve in which the tangent modulus increases. This might be an indication of the ease for cellulose microfibrils to slide among the incrusting polymer matrix. Consequently, a fibre variety with a high minimal tangent modulus will be favourable for high stiffness before rupture due to microfibril adaptation.

It is possible to obtain additional information on transverse mechanical behaviour of plant elementary fibres. These investigations are possible by nanoindentation and were studied by Gindl and co-workers [381] on a large range of cellulose fibres; by comparing transverse nanoindentation modulus with tensile longitudinal ones, the authors observed a high and pronounced degree of mechanical anisotropy for these fibres. The same approach was used by Bourmaud and Baley on sisal and hemp fibres [69] and Khaldi et al. [382] on alfa fibres. Despite the difficulty in sample preparation, this characterisation interestingly opens a window to an alternate, inverse method [383] to experimentally estimate the transverse stiffness of plant fibres. Transverse behaviour of fibres can also be studied through compression testing [384], especially in order to determine a transverse elastic limit and to highlight the high level of anisotropy of specific fibres.

As discussed, these tensile or nanoindentation tests are possible on both short and long plant fibres. They enable to obtain relevant mechanical information which is especially useful for designers and modellers. Elementary plant fibres are the basic reinforcement elements within a biocomposite and an accurate knowledge of their properties is preponderant for the development of the former.

3.2.4. Mechanical characterisation of plant cell walls

Small-scale experimental techniques, such as atomic force microscopy (AFM) or nanoindentation, were initially developed and applied to nanocomposites, and optical and medical materials. Progressively, their use was extended to a wide range of materials, and in the last 10-15 years they have allowed to investigate the plant cell wall mechanical properties.

Nanoindentation can be used to determine the longitudinal or transverse mechanical properties of natural fibres. The determination of the transverse modulus of plant fibres gives their stiffness anisotropy values as described previously [69,382]. Wei and Bhushan [385,386] performed nanoindentation tests on human hairs to point out the influence of structure, damage, treatments or soaking. Nanoindentation has also been used to obtained the mechanical properties of synthetic fibres, particularly glass fibres [387,388] or carbon fibres [389]. Regarding plant cell wall investigations, many authors studied the mechanical properties of wood cell walls by using nanoindentation. Gindl et al. [390,391] measured transversal and longitudinal moduli of various cellulose fibres origin using tensile tests and nanoindentation. Tze et al. [392] have shown a small length-scale effect on wood cell walls, and a decrease in modulus and hardness with increasing MFA determined using X ray diffraction. Wu et al. [393] evaluated elastic modulus and hardness of crop stalk cell walls using nanoindentation. They found that crop stalk fibres have better mechanical properties than wood or semi-synthetic cellulose Lyocell[©] fibres. Zou et al. [394] evidenced significant differences between the mechanical properties of bamboo fibre cell walls and bamboo parenchyma cell walls by using nanoindentation. For around a decade, our team has published several papers on plant cell wall mechanical properties through nanoindentation tests [21,69,127,395] on flax, sisal and hemp fibres. These studies highlight the utility of the method to enable comparison of cell wall stiffness and to show differences between both species [69] or cell wall structure or position within a stem [395,21].

On mature plant cell walls, the longitudinal nanoindentation modulus is generally between 15 and 22 GPa [390,395–397] and differences are often low between various natural fibres. Whatever the cell wall, wood or plants, the longitudinal nanoindentation modulus is lower than the modulus obtained with conventional tensile tests [395,398], but this is likely because the scales and the measurement modes are very different. The next section includes a detailed analysis of this difference between nanoindentation and tensile modulus. For example, good correlation is obtained between nanoindentation longitudinal modulus of flax fibres (17.97 ± 1.61 GPa [395]) with that of cellulose (18.2 ± 1.7 GPa exhibited by Gindl et al. [9]) and wood [399]. The differences between varieties could be induced by variations in the cellulose MFA,

the crystallinity of cellulose, and the cellulose:matrix volume ratio, as evidenced by Tze et al. [392]. As assumed by Konnerth et al. [396,398] and Gindl et al. [400], the hardness behaviour is dominated by polymers constituting the polysaccharide cell matrix, i.e. hemicelluloses and pectins. In contrast, the nanoindentation modulus is more linked to the properties of cellulose and to the MFA. Mechanical properties of plant fibres such as flax are mostly influenced by the S2-layer [149] and more specifically by its architecture. For flax, the S2-layer is constituted by cellulose microfibrils (around 70%) with a specific MFA (around 10°) covered by hemicelluloses (xyloglucan and arabinoxylan) which act as an interphase with the pectic matrix (rhamnogalacturonans, homogalacturonan and xylogalacturonan) [182]. The indentation hardness is generally between 0.25 and 0.4 GPa for wood [390,401] and flax cell walls [395,402]; the monitoring of this parameter is a useful way to estimate the evolution of the damage to the plant fibres after, for example, a process cycle within a polymer matrix. Indeed, understanding the mechanical properties of biocomposite constituents, especially cell walls, after a transformation cycle is a big challenge. Nanoindentation is a powerful tool that can be used to determine the in situ mechanical properties of composite fibres at the micron or sub-micron scale without any extraction or damage to the material. An attractive feature of this technique is that the measurements are made without requiring burning, chemical or mechanical modifications to isolate individual fibres as is required in elementary fibre tensile tests. These chemical and mechanical modifications change the mechanical properties of the vegetal fibres in poorly defined ways due to the sensitivity of plant fibres to chemical reagents and their low degradation temperature [403]. In this way, indentation modulus and hardness were measured on the wood particles before and after extrusion and injection by nanoindentation [404]. The indentation hardness results demonstrate wood cell wall hardening as a function of processing cycles, probably resulting of a crosslinking of both lignin and xylan polymers. Furthermore, Yildiz et al. [405] observed that the intrinsic mechanical properties of spruce wood samples decrease by increasing the temperature and duration of heat treatment. This was mainly correlated to a degradation of hemicellulose components. Hosseinaei et al. [406] showed a strong drop in the nanoindentation modulus of wood after hemicellulose extraction . They also related their results to a change in lignin arrangement, i.e. the lignin can

melt, coalesce and migrate from the cellulose microfibril surfaces into the cell walls because of a high temperature. Similar studies were performed on flax fibres to monitor cell wall properties after processing [402,407] or with recycling cycles [285,408]; a small decrease in nanoindentation modulus is generally noticed, except when shear rates are severe, as would be the case in injection molding processes [409]. Interestingly a decrease in flax cell wall hardness is noticed after processing, highlighting a higher sensitivity to process than wood cell walls.

Figure 30

Nanoindentation experiments demonstrate that stiffness decreases when MFA increases. Furthermore, nanoindentation tests are very sensitive to changes in MFA implying that samples need to be properly aligned with respect to the actual MFA in the indentation volume [396,411]. Eder et al. [399] showed that nanoindentation measurements are also highly influenced by cell wall composition and particularly the content of the polysaccharidic matrix. Thus, nanoindentation is a powerful tool to study the effects of wood modification on cell wall properties, and linking with the age or nature of wood [396,412–414]. Finally, methodologically speaking, it is commonly admitted that the radius of the elastically affected volume around the tip is about 3 times the residual indent radius for an isotropic material [399]. Due to the small thickness of wood cell walls, such as of wood or kenaf, stiffness results can differ according to the location of the indent in the cell wall [401]. The choice of the indent location is easier in larger S2-layers, such as of hemp or flax, and the uncertainties on results are then reduced. To improve the accuracy of nanoindentation measurements, it is possible to check the indentation position through AFM measurements; thus, nanoindentation systems including AFM equipment are now available and used for wood or plant cell walls characterisation [396,408,415]. Coupling AFM and nanoindentation gives access to information about indent by monitoring both the surface displacement during the recovery phase and the indent size after testing. Thus, Keryvin et al. [416] were able to determine visco-elastic parameters of flax cell walls. In the same way,

Tanguy et al. [101] evidenced indentation depth differences between flax and jute due to the specific microstructure of the two cell walls.

AFM investigations can also be performed to obtain mechanical informations at the cell wall scale. First experiments were developed in 1996 by Yamanaka and Nakano [417] and Rabe et al. [418] on wood cell walls. This method is called Force Modulation Microscopy or Acoustic Force Microscopy, where the AFM cantilever is used as a resonator, where frequency is a function of the interaction between the tip and the sample. It permits to map the elastic properties of the surface, thanks to a model based on the mechanics of contact, with the same resolution as topography measurements. Further developments were achieved by Clair et al. [419] and Nair et al. [420] by using 'resonant contact-AFM' (RC-AFM) on wood cell walls and nowadays, this technology enables to obtain fine and well-defined cartographies of cell wall stiffness. An example is given Figure 30.a. Recently, the new and promising PF-QNM technique has been developed and used on plant cell walls. Ren et al. [421] performed measurements of elastic modulus on secondary cell wall and the compound middle lamella of bamboo fibres. They found stiffness values of 21.3±2.9 GPa and 14.4±3.6 GPa, respectively, which agrees well with data measured by the nanoindentation technique. With the same aim, Arnould et al. [342] showed all the potential of this new technique by evidencing stiffness gradient on immature flax fibres (Figure 30.b).

In both nanoindentation and AFM techniques, the quality of the results is highly-dependent on sample surface preparation. Pathak et al. [422] compared nanoindentation stress-strain curves for mechanically polished, electro-polished and vibro-polished metal surfaces. They did obtain not suitable surfaces for accurate indentation tests. Qasmi and Delobelle [423] also tested metal samples and evidenced the influence of the roughness parameter on the standard deviations of the average values of nanoindentation modulus and hardness. Few studies exist on natural material but Zimmermann et al. [424] showed that a fine polishing process resulted in a very smooth wood sample surface that enabled superior AFM height and phase measurements compared to microtomed sections. Nevertheless, this conclusion must be moderated, as with optimal blade and preparation conditions, microtome cuts can enable experiments even in AFM PF-QNM mode [342].

These different developments, both in nanoindentation or AFM, show the interest of these two investigation techniques to estimate the elastic properties of plant cell walls. They cannot provide absolute values but suitable comparison according to the variety, the biochemical structure network or the thermo-mechanical stress suffered by fibres can be ascertained. Thus, the different study scales are strongly complementary and collected informations enable a global understanding of the cell wall mechanical behaviour.

To conclude this section, Table 4 proposes a summary of the various mechanical data that can be obtained at the various investigation scales.

Table 4

Whatever scale of experimental testing, a large range of the fibre's mechanical properties can be obtained; some of them can be calculated by different routes. To extend the panel, the composite scale has been added. Through inverse calculation methods, some of the fibre's mechanical properties can be estimated, regardless of the fibre distribution and orientation within the composite. This latter method enables to average data on a large number and types (e.g. lengths) of fibres, rather than on a limited number or type of elements, as is the case by elementary fibre tensile or nanoindentation testing.

3.3. Experimental characterisation

Given the complexity of the structure and constituents of the plant fibres, the method of experimental characterisation is of particular importance. In this section, we will endeavour to highlight the importance of the scale of measurement by taking the example of the measurement of the stiffness of the fibres. We will discuss the significance of the experimental method chosen by comparing the different protocols used for the determination of the plant cell walls MFA as well as their biochemical composition, both impacting the stiffness measurement (Section 3.2) . We will conclude this section by questioning the errors induced by

approximations of measurement or by the interpretation of the results which can vary according to the view of the experimenter or the characteristic elements of the walls stressed during these measurements.

3.3.1. Effect of the investigation scale on measured mechanical properties: the case of stiffness

The plant cell wall modulus can be obtained through various investigation methods. In this section we discuss the significance of these different values, and if possible identify the most appropriate one. Stiffness measurements made using tensile, nanoindentation and AFM methods will be compared and discussed. In addition, the inverse method, using unidirectional composite properties, will be cited and discussed, alongside original methods based on vibrational fibre behaviour.

Longitudinal modulus of elementary plant fibres has been widely studied by tensile tests. As described previously, this method enables obtaining Young's modulus of long plant fibres such as hemp, flax or ramie. For short fibres specific devices were developed and validated by wood science research teams [113,115]. On long phloemian fibres, tensile tests are generally performed by using a nominal length of 10 mm; for an accurate measurement, high precision loading cells are preferred, they exhibit maximal values included between 2 and 20 N [358,149,425]. Experimental conditions of these tensile tests on elementary plant fibres are detailed in the XPT 25-501-2 standard [426] dedicated to flax fibres. This standard includes the description of the calculation of the load cell compliance which is necessary to correct the measured displacement. This correction must be performed after calibration. Alternative non-contact methods, such as digital image correlation [427], provide interesting routes to measure deformation. The standard recommends calculation of the fibre longitudinal modulus in the last part of the stress-strain curve, after the micro-fibril loading and realignment phase. As discussed previously, this method is debatable as indeed, the modulus value takes into account both the elastic and the inelastic response of the fibre. Moreover, this apparent tangential stiffness is calculated at a high strain level, which is difficult to link to effective deformation within a

composite. Nevertheless, for these specific conditions, it is possible to obtain reproducible stiffness values on elementary plant fibres. As described previously (Section 2.2.1), Young's moduli for flax, hemp and ramie fibres are generally between 40 and 60 GPa, 20 and 40 GPa and 30 and 50 GPa, respectively. Prior to measurement, fibre diameter is obtained by microscopic analysis, taking into account several measurement points along the fibre length but the lumen size is neglected which can possibly induce an underestimation of the fibre apparent stiffness [428]; this point is not a real problem for fibres having high cell wall thickness such as flax [429] (except for hollow fibres which have suffered any growth accidents), but can be questionable for heterogeneous [21] or large-lumen fibres [430]. Nevertheless, biocomposite mechanical behaviour is governed by both polymer matrix and fibre components, and the reinforcement object is the whole fibre (including the unfilled lumen and cell wall), consequently the use of fibre global stiffness in micromechanical modelling estimation can be validated.

With the development of local investigation methods such as AFM and nanoindentation, cell wall longitudinal stiffness can also be measured using these equipments. Indeed literature assumes that the S2-layer is the principal component governing fibre mechanical behaviour [149,66] and as a first approach it seems reasonable to investigate S2-layer mechanical properties.

In nanoindentation, tests are performed with a Berkovich-type indenter loading the wall at an angle of approximately 25°. Thus, a complex loading condition exists under the indenter that yields a reduced modulus that depends not only on the longitudinal modulus but also on the (lower) shear and transverse moduli [411]. Indeed, as evidenced by Baley et al. [27], flax fibres are highly anisotropic, and their transverse modulus is estimated to be 8 GPa. This tendency is confirmed by the nanoindentation results obtained with other vegetal fibres. We have obtained a transverse modulus of 5.0 ±1.5 GPa and 3.9 ± 0.9 GPa, respectively, for hemp and sisal fibres [2]. This important anisotropy induces an underestimation of the longitudinal modulus. In the same way, Gindl et al. [8-9] indicated that longitudinal modulus of wood cell walls obtained by nanoindentation is considerably lower than the tensile Young's modulus or model calculations. Anisotropic models for the reduced modulus obtained by nanoindentation have been successfully applied in the case of the softwood S2-layer by Jäger et al. [411].

Table 5

Fibre moduli obtained by tensile, nanoindentation and AFM mapping on flax, bamboo and wood cell walls are presented in Table 5. Although similar stiffness' are measured by nanoindentation and AFM mapping, it is not the case for tensile measurements; in line with previous explanations, tensile modulus is much higher for the whole cell walls. Some authors have tried to correlate tensile and nanoindentation stiffness. Gindl et al. [381] (Fig. 31.a) presented a correlation curve for different regenerated cellulose fibres and Tanguy et al. [101] proposes the same approach for a large range of plant fibres (Fig. 31.b).

These correlations are interesting and can be used to estimate the stiffness of fibres that are too short for tensile measurements. Due to the specific correlation curve shape with a kind of asymptotic behaviour for high tensile modulus, one can notice that the gap between tensile and nanoindentation/AFM modulus increases when fibre MFA decreases (Fig 31.b and Tab. 1). Indeed, the higher the MFA, the lower the mechanical anisotropy, due to a lower longitudinal modulus and a higher transverse modulus. Nevertheless, if they are relevant in case of morphologically similar fibres, discussion is open when comparison is done between several fibre species (Fig. 32.b). Indeed, these fibres have different lumen size and a same fibre can exhibit large cell wall stiffness and low tensile modulus due to fibre morphology, in the same way main factors like MFA, presence of bundles, cellulose content or crystallinity should be taken into consideration in tensile or nanoindentation analysis.

Figure 31

Thus, it is possible to determine plant fibre cell wall stiffness by using different investigation techniques at the macro, micro or nano scale. Nevertheless, at the composite scale, the tensile

method is best to obtain the whole fibre apparent tangential modulus. Nanoindentation or AFM mapping can be used to measure cell wall stiffness but due to the loading mode and fibre anisotropy, these methods don't provide absolute values but do provide pertinent data to highlight stiffness gradients or to compare cell wall mechanical properties. In the last few years, complementary methods have been developed by using force vibrations [431,432], light diffraction [433] or resonant ultrasound microscopy [434], but they are not yet mature for plant fibre stiffness measurements.

3.3.2. What is the suitable method for MFA measurement?

Due to the importance of cellulose microfibrils orientation on the mechanical properties of plant cell walls [220] many techniques for measuring MFA in plant cell wall layers have been developed during the last decades. Thanks to the pioneering work of Cave and Meylan [435,436], wide or small angle X-ray diffraction is the most widely used technique but other alternative methods exist, mainly based on microscopic observations. Among these latter, some use the optical properties of crystalline cellulose such as polarised light microscopy (PLM) and others enable to visualise fibril orientation by direct or indirect observations. Examples include iodine precipitation [437] fungi-rot treatment [438], fluorescence microscopy [439] or transmission electron microscopy (TEM) [207]. In this section, we will briefly describe and compare the principal methods, and evaluate their main advantages and drawbacks.

Polarisation microscopy was the first technique [440] used for the measurement of wood cell MFA and it is still used today. The method is based on the fact that cellulose is partially crystalline and that microfibrils within each secondary wall layer are bi-refringent, enabling an identification of the main secondary cell wall layers, which have different brightness at different orientations of the section. By PLM, it is only possible to measure MFA in longitudinal sections; cross-section layers are not large enough and the obtained MFA is consequently an average value of the whole secondary wall [440], including S1 and S3 layers and not only S2. The main drawback of PLM is the fact that the light passes through two walls in which the microfibrils form opposite sides of the spiral. Preston [440] overcame this difficulty by cutting the tracheids

longitudinally to leave only one wall. Another solution is to fill the cell lumen with mercury and viewing reflected light using epi-illumination [441] or observe the elementary layer MFA by observing it through a pit aperture in the opposite wall of the cell [442]; this latter method requires to remove the pit membrane by maceration prior to analysis. In the same way, the orientation of the pit apertures is known to often follow the orientation of microfibrils, and has been used by direct observations to measure MFA [443]. Nevertheless, this orientation of adjacent pits may differ within the same cell wall, inducing some interpretation mistakes. Huang et al. [444] showed that pit-aperture techniques worked better for latewood than earlywood, probably because pit apertures tend to be rounded in earlywood, making measurement of orientation difficult. This difficulty was also underlined by Wellwood et al. [445]**.** Latewood tracheids are preferentially examined because the pit apertures are more elongated and hence it is easier to measure the orientation. Moreover, the presence of pits out of the plane of the section could have influenced the results [446]. In spite of these drawbacks, pit aperture method results exhibit interesting correlation with X-ray diffraction measurements on Pinus elliotti [447].

Because cellulose is semi-crystalline, the MFA of the S2 layer can be measured by X-ray diffraction. XRD is the most convenient and widely used method for MFA estimation. The recent development of automated devices such as SilviScan have produced large datasets [448], especially in wood science. MFA estimation by XRD is based on the theoretical relation between T (full width at half maximum on the spectra) and the mean MFA and by the shape of the intensity distribution of the (002) arc. XRD parameters were extensively studied by Cave [212], Meylan [436], and Evans [449]. The method proposed by Meylan [436] requires calibration against other methods, while the variance method proposed by Evans [449] is directly related to MFA but with the disadvantage that precision is less at very high angles because of the relatively weak diffraction signal from juvenile softwood. XRD measurement are validated considering that all microfibrills are crystallographically identical and that the whole cell wall consists of an elementary homogeneous layer of microfibrils (S2-layer) embedded in a non-crystalline matrix. Thus, for interpretation, fibre is supposed to be perfectly cylindrical, with a constant MFA in the cell wall thickness and within the scanned volume. Depending on the analysed object's structure, MFA could be an average value from different cell wall layers.

Moreover, in most of studies, fibres bundles [20] are studied; they contain a significant part of middle lamella, having a potential impact on measured values. For X-ray diffraction, the choice of analysis method may influence results. Yamamoto et al. [450] developed a specific analysis method that gave better results, especially for reaction wood. XRD investigations can be performed using small (SAXS) or wide-angle XRD; Lichtenegger et al. [214] have compared the two methods and conclude that they lead to the same results. SAXS has the advantage of higher spatial resolution, allowing measurement on elementary cells, which is useful for hardwoods to differentiate cell types, although it requires a synchrotron X-ray source. In comparison to the PLM method, literature diverges: while Peter et al. [451] find same results for Pinus taeda samples over a large range of MFA, other authors find strong differences between the two methods on Picea mariana [452] or Picea abies [453,454]. The difference were attributed to the effect of S1 and S3 layers on PLM measurements.

Near-infrared (NIR) spectroscopy can be used to predict MFA by scanning of wood surfaces on the radial longitudinal face of increment cores using multivariate modelling techniques [455]. This method is interesting and quite easy to perform but a strong correlation between density and MFA exists [455]. Thus, MFA estimation must be performed when density variation is small, this value being uncertain for density sample under 0.5 g/cm3. Thus, the prediction of MFA by using NIR spectroscopy is problematic for juvenile wood [456], confirming the difficulty to obtain relevant MFA for young wood. Nevertheless, this method was found to be in excellent agreement with MFA determined by X-ray diffraction on wood kraft pulp [455]. In addition, Raman microscopy has been used by Thygesen to study the MFA in dislocation areas of hemp fibres [457]

Other marginal methods based on direct observations can be used for MFA estimation. The precipitation iode method [437] can be used to visualise MFA. It is based on the precipitation of iodine crystals within the cell wall, enabling to make images of the cavities produced by the crystals to perform fast MFA estimations [458]. Several authors evidenced an interesting correlation between the iode method and XRD [436,459,460]. It is also possible to use microscopic fluorescence in order to estimate MFA thanks to confocal measurements. However, this method has the disadvantage of being relatively slow [439], but is generally in good

agreement with XRD [461]. By using a calibration grid, transmission microscopy (TEM) is a good alternative for direct measurements. It provides suitable information at the elementary cell wall scale [446]. Nevertheless this method requires extensive sample preparation due to the necessity to prepare ultra-thin cuts in the longitudinal direction. Ultraviolet illumination [462] combined with phase contrast microscopy can also be used to observe micro-checks in the fibre walls, as well as ellipsometry [463] .Interestingly, this latter method is independent of fibre orientation and doesn't require elementary cell walls, making it ideal for measurement of plant pulp or bundles. Finally, the original soft rot cavity method, based on the formation of cavities by fungus along the microfibrils can be cited [438]; this method is easy to perform but has the disadvantage of requiring a relatively long time (6 –14 weeks) for the fungus to produce sufficient cavities that are relatively coarse in size.

These different techniques and methods all enable to estimate MFA but also have some drawbacks. They must be selected according to the nature of the sample as indeed some parameters can affect the accuracy of the measurement. On widely used methods such as PLM and XRD, investigations are mainly performed on whole fibres or even on bundles; thus, presumed S2-values can be biased by overlapping between S1, S2 and S3 layers due to the relatively thick sections. In case of measurements on fibre bundles, estimated MFA are an average value of the different cell walls including fibres but also pectic cements. Consequently, some of these techniques are more suited to quantitative applications while others are used for simple imaging. Moreover, many methods are time consuming because the extreme variability of natural material and sample preparation; it is the case for PLM, TEM and iode method. In contrast, X-ray diffraction provides accurate results, at low cost, minimal preparation and short observation times. The main drawback to the X-ray method has been the interpretation of the diffraction patterns in terms of microfibril distribution.

3.3.3. Biochemical composition: many approach for many results

As described previously, plant fibre cell walls are mainly constituted of cellulose, non-cellulosic polysaccharides (NCP), water, lignin, proteins and some minor fractions of lipids and waxes.

The relative quantity of these components can vary considerably according to the plant species but also, as demonstrated on flax, with the variety [20], the cultural practise [464], the growing conditions [59], and the age and maturity of the plant [465]. This cell wall composition plays an important role in plant fibre mechanical behaviour [103]. Therefore, determining composition would enables better understanding of potential differences between fibre mechanical properties. Three main methods can be used to identify and quantify the cell wall constitutive polymers. Two of them are based on chemical extractions and the third is a global chromatographic method. Firstly, we propose to focus on the two methods based on successive chemical extractions and take the example of flax fibres due to the availability in literature of comparable data for these fibres.

The scutched fibres, corresponding to bundles of elementary fibres, undergo first a step of elementarisation thanks to three washings with water at room temperature, before being stored in distilled water. This first step makes it possible to remove retting and scutching residues [466]. Then, the remaining cortical residues are removed by extraction with boiling distilled water in three sequences (1.5hr one and then 1hr twice). Finally, the pectins of the middle lamella are extracted by a boiling calcium chelator, corresponding to disodium ethylene diamine tetra acetic acid of 0.25% concentration (0.25%, EDTA, Na$_2$) for 1 hr. This last extraction is followed by two stages of rinsing with boiling water for 1 hr each. The calcium chelator makes it possible to break down the calcium bonds, releasing the Ca-pectins and thus enabling to obtain the elementary fibres by decohesion thanks to integrity disruption of the middle lamella. After this preliminary steps, successive chemical extractions are performed, dried fibres residues are weighted before and after extraction to quantify the weight fraction of each main component, this latter being associated to each chemical extraction. Two main methods exist, using different solvents and concentrations: the method developed by Van Soest [467–469] and the second one called HCl/NaOH [470]. These two methods are detailed in Figure 32.

The Van Soest method [467–469] consists of two successive extraction steps. The first is made from a neutral detergent composed of ionic agents sodium dodecyl sulphate (30 g / L),sodium borate (6.81 g / L) and phosphate Disodium dihydrate (4.56 g / L) and chelatant agent EDTA

(18.61 g / L). The second is made with an acid detergent composed of cetyl trimethyl ammonium bromide (20 g / L) in 0.5 mol / L H_2SO_4. Each extraction step is carried out for 1 hr at 100 ° C and followed by two successive washes of 1 hr with boiling distilled water. Neutral detergent and acid extraction are supposed to extract successively pectins and hemicelluloses polysaccharides (NCP), respectively.

The second method (so called HCl, NaOH) [470], consists of two successive extractions from a mild acid reagent (0.015M) followed by a basic reagent (1.5M NaOH / 100mM NaBH4) [15-17]. The two extractions are carried out for 1 hr at 100 ° C and followed by two successive washes of 1 hr with boiling distilled water. High temperature and a neutral detergent (method 1) or HCl reagent (method 2) make it possible to extract the encrusting polysaccharides belonging to the wall matrix (essentially the S2). Then the acid detergent (method 1) or the NaOH reagent (method 2) extract the encrusting polysaccharides from the swollen walls that have strong interactions with the cellulose microfibrils. The latter have a structural role in the S2-wall. The mass of dry matter lost after each extraction is estimated after drying at 80 °C for 12 hours in a vacuum oven.

Figure 32

In order to compare the two extraction methods, three batches of scutched flax were analyzed by Lefeuvre [465]. These results show a significant loss of mass during the extraction with acid detergent of the Van Soest method (19%) compared to the NaOH extraction (HCl/NaOH) method (9%). Visually, the fibres exhibit a greyish color after acid detergent and a very brittle behaviour, falling into fragments. On the contrary, with the HCl/NaOH method, following the NaOH extraction, the fibres are white and keep their lengths. Thus, it has been found that the Van Soest method causes a degradation of the cellulose and is too aggressive for the flax cell walls. Consequently, NCP contents are higher with the Van Soest method estimation [125], compared to HCl/NaOH one [471]. Thus, although the Van Soest method is widely used and could be automatised thanks to the commercialisation of specific equipment, the HCl/NaOH one

has the advantage to be less aggressive and more selective, enabling to differentiate matrix and structuring polysaccharides, these latter can be linked to the mechanical performance or fibres. A global estimation of components such as Van Soest method is not well adapted for a fine and accurate NCP identification in order to link cell wall structure and mechanical performance.

Figure 33

After the extractions, the reagents, as well as the first water wash, can be recovered for analysis. The quantities of total and acid sugars can be determined by colorimetric assays: the Dubois method [145][18] is used for total sugars and the Blumenkrantz method [144] is used for for acids. This chemical analysis makes it possible to find the concentration of total oses with the Dubois method and uronic acid with the Blumenkrantz method from the measured absorbance [20]. Due to some reported lack of specificity of those spectrophotometer based methods, a possible additional investigation could also be performed by chromatography on remaining reagents in order to identify each elementary sugar which cannot be performed by the colorimetric method, and therefore helps in accurately describing the cell wall composition.

The third method to estimate the biochemical composition of plant fibres is based on chromatographic method. Amongst others, we can cite the PACE method [472,473] or the alditol acetates one [474] where the pentose or hexose monosaccharides or oligosaccharides can be derived and analysed by gel migration or Gas Chromatography. It seems from literature that the chromatographic method using High Performance Liquid Chromatography (HPLC) is widely in use and more details are given below for it (Fig. 33). Scutched fibres (a few grams) are ground in order to limit the impact of the natural variability, with care paid in the limitation of the heating created by the milling process to avoid irreversible thermal denaturation of the molecules that could bias the subsequent analysis. The powder obtained is then hydrolysed with strong acid coupled with heating above 100°C in order to break the polysaccharide chains and obtain elemental monosaccharides, also named as sugars [415]. These monomers are

then identified and quantified by HPLC. This method requires some knowledge about the biochemical structuration of the walls in order to assume precisely which elementary sugar corresponds to each of the polysaccharides constituting the walls. Indeed, this technique is well-accepted and accurate, but although the total amount of each sugar can be quantified, no direct indication about its location in the cell wall is obtained. By way of example, glucose is generally considered to be the constituent monomer of cellulose; its rate therefore makes it possible to know the rate of cellulose of the fibres studied. Then, in the same manner as for the two previous techniques, the Klason lignin can be quantified by calcination (Fig. 32).

3.3.4. Error induced by measurement interpretations: example of fibre's morphology on stiffness calculation.

Experimental testing is highly dependent on a large range of intrinsic and exogenous parameters. It should also be noted that the talent of the operator plays a major role. For plant fibre tensile characterisation, Müssig et Haag [358] highlighted the importance of gauge length, testing speed, environmental conditions, compliance of the testing machine, clamping mode and the way and the location of the CSA calculation. Among these parameters, the estimation of the diameter is probably the most discussed and controversial due to several reasons.

Many authors have showed the link between diameter and mechanical properties of plant fibres. The ultimate tensile strength (UTS) is shown to decrease when the fibre diameter increases for flax [375], hemp [70], jute [475] or sisal [111]. This phenomenon can be explained by Griffith's theory [476] which explains that the strength of a material is dictated by the presence, and in particular the size, of microscopic defects. The larger the flaw in a fibre, the lower its tensile strength, such that when the fibre diameter increases, the probability of the presence of a critical defect increases, resulting in a higher probability of premature failure [371]. The same tendency has been evidenced on the elementary fibres Young's modulus; several papers have reported the decrease of the longitudinal Young's modulus as the apparent diameter of flax [429], hemp [67] or nettle [477] fibre increases but in this case, Griffith's theory does not provide a complete explanation for the observed behaviour. In the literature, the diameter dependence

of the fibres' stiffness is often attributed to an over-estimation of their effective CSA, and consequently to uncertainty about the diameter measurement.

Thus, regarding the estimation of a true diameter, the main difficulty, in case of plant fibres appears to be the choice of the best suitable method to correctly determine the fibre diameter. Some authors have compared stiffness values of elementary fibres by measuring diameter between the test or close to the rupture zone. Duval et al. [67] exhibited a strong dependence between stiffness and diameter with this latter choice whereas Charlet et al. [478] didn't evidence any difference between the two methods. Errors in measurements can also be a first order parameter in modulus variations. Lefeuvre et al. [103], thanks to a deep analysis, showed that on average, 78% of Young's modulus uncertainty and 93% of strength at rupture uncertainty was introduced by the CSA measurement. This important impact of CSA must be linked to the diameter determination which is generally performed thanks to optical observation, assuming that the fibre is a perfect cylinder. However, flax fibre's sections were shown to significantly vary along their length, with a coefficient of variation for the diameter about 20% [479,480] and the fibre diameter is generally obtained thanks to an average of several measurements along the fibre length. Lefeuvre et al. [103] studied the influence of the number of measurements points on the value reliability; they finally chose 6 spots, taken at equivalent distance along the fibre. Moreover, fibres whose diameter measurements varied by more than 5 μm along the gauge length were rejected. A significant decrease in the Young's modulus standard deviations were highlighted compared to the literature data, showing that careful measurement could greatly reduce the uncertainties and make it possible to provide more reliable data.

Uncertainty in CSA measurement was studied by a number of authors by proposing or comparing alternative CSA estimations. For example, Thomason et al. [481] showed that cross-section values obtained from fibre diameter measurements were more than double the values obtained from actual observation of cross-sections of the same sisal fibres inducing a pronounced underestimation of the fibre stiffness. In the same way, Haag and Müssig [358] compared flax bundles tensile strength obtained from three diameter measurement methods (light microscopy, high resolution flat-bed scanning, and laser-based fibre dimensional

analysis). They showed that the CSA method alone is introducing up to 300 % of variation in tensile strength data. Nevertheless in these two cases, measurements were performed on fibre bundles and not on elementary fribres. The high discrepancy in bundle shape can lead to strong CSA differences, according to the selected measurement method. In the case of elementary fibres, the measurement error is less pronounced. Charlet et al. [482] compared CSA values obtained from elementary flax fibres cross-sections using diameter measurements; they showed that a hexagonal geometry is not a better approximation of the real fibre shape than a circular one and that the dispersions in fibre dimensions and properties largely exceed the error generated by approximating the fibre shape as a circle. Nevertheless if bundles are tested, the diameter measurement is generally not reliable and alternative method such as Fibre Dimensional Analysis must be preferred [483]. The question can be also asked for irregular elementary fibres; Marrot et al. [21] performed tensile tests on elementary hemp fibres and showed that no matter the location in the stem cut, cell-form factors (CFF) are far from 1 (CFF=$4\Pi A/P^2$ with A = fibre area and P = fibre diameter). The CFF is lower for internal fibres (0.66) than for external fibres (0.77). It means that fibres are elongated or slightly flattened, and internal fibres are stretched further than external fibres. For flax fibres, Alix et al. [484] found that CFF depends on the flax variety; it can also vary according to growing conditions [59]. For the Hermes variety, CFF were between 0.9 and 1 corresponding to hexagonal and circular shapes respectively, whereas CFF were close to 1 for the Oliver variety (mainly circular shapes). In the case of hemp, the lower CFF values highlight the considerable scattering in fibre morphology. Thus, because of the non-circular geometry, the diameter measured from longitudinal observation with the optical microscope can correspond to the minimal Feret diameter [429] and then be underestimated. Finally, the difficulty in measuring fibre diameter greatly depends on the observation angle. Ilczyszyn et al. [485] used sample pictures taken at different orientations to reconstitute by numerical imaging the real profile of the fibre cross section. This method brings more accuracy, but is time-consuming due to the number of fibres required for a tensile test. Moreover, this last method needs more handling, which a potential source of defects creation and consequently, alteration of cell wall mechanical performances.

Regarding mechanical properties calculation of the elementary fibres, there is a debate about whether or not to account for the central fibre lumen. Nevertheless, its experimental determination is not obvious, cutting techniques using microtome can induce damage and deformation, SEM observations can induce deformation or shrinkage of a fibre, due to the use of low vacuum conditions, and produce significant surface modifications due to electron beam damage. Non-destructive methods such as X-ray tomography can be performed but they are time and resource consuming and not well-adapted to the testing of a large number of fibres. As underlined previously, the lumen size considerably varies according to the plant species, representing only a few percent of the fibre section for flax [56], hemp [21], ramie [57] or bamboo [48] whereas it can be close to 20 to 30% of the overall section for sisal [56], jute [56] and abaca [99,45] or 60 % and 90% for kenaf [84] and kapok [82], respectively. Thus, depending of the lumen size, fibre cell wall stiffness or strength can be highly underestimated when CSA is deducted from the apparent diameter. Placet et al. [380] calculated the resulting error for hemp fibre stiffness and showed that the assumption of a cylinder without a lumen can lead to a 15-25% under-estimation of the longitudinal fibre stiffness for a surface area ratio of the lumen between 10% and 20%. Notably, there is evidence of a significant change in lumen shape along the length of hemp fibres [486], meaning that the lumen size in not homogeneous in all transversal section of the fibres. The same variation can arguably been hypothesised for other lignocellulosic fibre botanical origins. Even so, the majority of authors choose to optically measure fibre diameter for CSA calculation, both for the speed and simplicity of measurement but also by considering that within a composite, the whole fibre, including lumen, must be taken into consideration and represent the real reinforcement object which is not limited to only the cell walls.

3.4. Pertinent fibres for high-performance composites

3.4.1. Importance of retting and mechanical treatments

Among the number of parameters investigated in this review, we have discussed on several occasions the impact and influence of retting on fibre quality. After crop pull-out, retting is the

first step in the processing of fibres and its influence both on fibre and composite properties is essential to understand. Figure 34 synthetises the potential consequences of the retting parameters on both fibre and composite properties.

Figure 34

As described previously, dew retting may be divided into two spatio-temporal steps. First, the epidermis and cortical tissues of the stem layered on the soil are colonised by fungi which release several enzymes that degrade pectins and more generally polysaccharides [487,23]. As a result, epidermis and cortical parenchyma are partly degraded and the fibre bundles split [488]. Calcium pectates are considered to be retting resistant and are the limiting factor of retting [489]. In a second step, the fungi colonise the fibre bundles where the complex matrix present in the fibre junctions and enriched in pectins might be partly degraded [319,490]. Such a two-step retting facilitates the fibre decortication [255,248] and enable an improvement of the elementary fibre mechanical properties as exhibited by Martin et al. on flax [24]. On the other hand, if continuous rains occur at this latter retting stage and do not allow the harvest, then the fungi continue their development within the elementary fibres, initiating rotting. Indeed, the fungi undergo the degradation of the cellulose microfibrils in the successive cell-wall layers, due to the secretion of glucanase and cellulose enzymes [491], significantly degrading the fibre's tensile performances [249]. This step is called over-retting. Therefore retting is a critical agricultural process, determining the easiness of division of the bundle and the surface quality of the so-called technical fibres. Some of the variation in the degree of retting can be reduced 1) by modifying the subsequent mechanical treatments of the straw (breaking, scutching and hackling), which separate the bast fibres from the woody core and 2) by degumming treatments during the wet spinning-process [492]. At the end, partially degraded bundles constitute the so-called technical fibres that are a mixture of a certain number of fibres (1 to 10) with loose cohesion between each other and the debris of cortical tissues.

At the composite scale, Bos [278] has shown how flax fibre bundles can reduce the mechanical properties of composite materials. Rask et al. [493] studied the damage mechanisms of unidirectional flax-polypropylene (PP) composites using X-ray diffraction, and concluded that well separated fibres are recommended for composite reinforcements. Andersons and Joffe [494] made similar conclusions by demonstrating that a probabilistic model, assuming perfect separation and regular spacing of fibres, yields an upper limit on the strength for unidirectional flax composites. The influence of the dispersion of elementary fibres on the mechanical properties of flax/ polypropylene composites has also been shown [262]. Morphological analyses highlighted the importance of a hackling step for fibre dispersion; this process reduces the number of bundles in the final composite. Fibres subjected to combing have been used to manufacture composites with a separated fibre content similar to that found with glass fibres. The study of damage in polypropylene composites reinforced by injected flax fibres [367] has shown, as for traditional composites, a significant skin/core effect. Shearing effects close to the mould result in high orientation of the fibres in the flow direction in these regions, whereas in the core, as a result of divergent flow and lower shear, the orientation is more isotropic. This results is more fibre bundles in the core which can cause premature failure in this region and a drop in composite strength and failure strain. Tensile tests performed inside a scanning electron microscope confirmed this effect, showing crack propagation within clusters of fibres. Thus fibre clusters and bundles promote damage initiation and fracture propagation. This skin/core effect has also be showed by Gallos et al. [495] on hemp-polycaprolactone (PCL) composites; a dependence on fibre content was highlighted with a large skin fibre fraction for reduced global fibre content. In addition, the authors showed that porosities and connections between fibres evolve similarly at all fibre content.

Furthermore, the quality of the fibre's surface can strongly influence composite performance. In case of sub-, normal or over-retted fibres, quality of the surface differs significantly in terms of surface composition, roughness and presence of aggregates [249,496,497]. The properties of the zones between adjacent fibres in a bundle are also variable as they depend on the degree of retting. Le Duigou et al. [497] studied the interfacial properties of sub- and normal retted flax fibres with a polylactic acid (PLA) matrix, and showed that the outer fibre layer topography or

roughness is influenced by retting and extraction processes, due to the presence of rest of junction or even cortical tissues on the primary cell-wall. Sub-retted fibres exhibit a notably rougher surface which should act as a defect at the fibre/matrix interface.

Thus, in order to improve composite quality and performance it is necessary to improve the separation and dispersion of fibres by optimising not only the retting but also the extraction process and manufacturing conditions.

3.4.2. Towards relevant mechanical characterisation

According to the nature of the research, the mechanical performance of the cell walls can be interpreted in different ways. We have seen previously that mechanical characterisations re possible at different scales. They can be conducted at the scale of the plant cell wall up to the scale of the stem. However, the study of the mechanical properties on the scale of the elementary fibre is the one that most allows to get rid of uncertainties related to the quality of the middle lamella or to the discontinuity of the fibres. This mode of characterisation requires time and an important know-how, but remains incomparable to quantify the mechanical performances of the plant fibres. On the other hand, it is necessary to be certain that we are dealing with elementary fibres, and the use of polarised light makes it possible to discriminate fibres and to validate the tests. During these tests, the quality and the degree of filling of the fibres are also taken into account. Depending on the nature of the species considered, the geometry of the fibre, its degree of retting, growth conditions or maturity, both the degree of maturity of the walls or the size of the lumen may vary. They can significantly influence the mechanical performance of the fibre object and particular attention must be paid to the quality of the selected fibres so as not to lead to erroneous conclusions as to the performance of the fibres tested. The experimental parameters are also predominant, and some standards exist [426] to govern these tests and to ensure their validity whatever the equipment used. However, the experimenter's know-how plays an important role, particularly during the phase of extraction, selection and measurement of elementary fibres.

In order to reinforce composite materials with plant cell walls, it is necessary to ask the question of the relevant object to analyse. Should the mechanical characterisation be done on the scale of the wall, the fibre or the bundle? The answer to this question depends not only on the material produced, but also on the nature of the fibre and the species under consideration. The relevant scale may differ depending on if we are dealing with bundles of vascular coir fibres in which the fibres are assembled in a very cohesive manner, of highly-lignified jute or sisal bundles, or highly individualised hackled flax fibres. In spite of the shear induced during the manufacturing of injection-extrusion moulded composites, it will be in some cases very difficult, if not impossible, to divide the bundles which leads to preferring this scale to characterise the reinforcement objects. Castellani et al. [498] proposed a breakage model of the bundles, depending on the lignin content but also of the tested species. Moreover, as mentioned above, it is in some cases almost impossible to characterise the elementary fibres for practical reasons linked to their short length. The relevant measurement scale may also differ depending on the treatment of the fibres and the quality of their extraction. In the case of flax, modest retting, conventional scutching or hackling will not lead to the same degree of fineness [262]. This will be found at the composite scale, so their quality will be strongly influenced by the initial state of the fibres. The same applies to the biochemical treatments undergone by fibres such as alfa to facilitate their extraction [47]. Their treatment intensity leads to very different levels of division of the bundles. Thus, depending on the nature of the fibres under consideration, characterisation of the bundles may be preferred to that of the elementary fibres and vice versa. This may also depend on the nature of the manufacturing process used. During a process cycle, whether it is a thermosetting or thermoplastic matrix composite, the shear rates vary greatly. They can range from a few s^{-1} during film-stacking compression moulding processes [499,500] to more than 10000 s^{-1} in the case of injection moulding [402]. The latter will naturally lead to more marked division of bundles which may lead to the need to know the properties of the elementary fibres rather than those of the bundles. In materials such as non-woven flax mats [147], given the low level of splitting of the tows used, we may encounter some elementary fibres, but primarily bundles, and sometimes even straws. This heterogeneity has an important impact on the performance of the materials and in particular when they have low densities. In this case, the

quality of the composites is strongly linked to that of the polymer bridges with the fibres and the bundles, the interfacial phenomena and the mechanical performance of the reinforcement objects, it is therefore necessary here to take into account both the performances of the elementary fibres but also those of the bundles for a good understanding of those of the composite.

For optimal mechanical characterisation, experimental parameters and environmental conditions are also important. The humidity and temperature during the tests must be controlled. Their values are imposed by the standards. Even more than for synthetic fibres, plant cell walls have a high sensitivity to these factors, whether in terms of mechanical performance or dimensional stability. As already mentioned, the control of displacement during a tensile test must be optimal and the compliance of the force sensor must be taken into account during the calculations. The positioning of the objects during the tests is also a first order factor, in tension, the elementary fibres or the bundles must be well-oriented with the axis of stress. This is also true at the cell wall scale during AFM or nanoindentation characterisation. In nanoindentation, an inclination of the fibres, even by a few degrees, can lead to significant differences in modulus [411] because of the very low transverse stiffness of the fibres which greatly influences the measurement. The quality of surface preparation as well as edge effects are also points to be taken into account during a nanoindentation test [342,410].

3.4.3. How to define at best the plant fibres? Reliable parameters for a use as composite reinforcements

In this section, we will focus on defining the relevant parameters to be taken into account when using plant fibres as composite reinforcements. The mechanical performance of a composite material are conditioned by those of the matrix and of the fibre, but also by the quality of the interface between the two components, which will play a major role in the transfer of load between these two components. Consequently, we will focus here on the intrinsic characteristics of the fibre and the influence of the fibre/matrix interface.

At the scale of the fibre, the surface properties are paramount as their quality of these can greatly influence that of the interface. This has been demonstrated by Le Duigou et al. [497] on fibres having surface impurities. Residues of middle lamellae on the fibre surface can penalise the quality of the interfaces with the composite. Differences can also be observed depending on the nature of the fibres. Because of their different biochemical compositions, flax and hemp possess properties of surfaces that are not the same [501–503]. Several methods like dynamic contact angle (DCA) or inverse gas chromatography (IGC) have been widely used and compared when aiming at evaluating surface physic-chemical properties (polarity, dispersive surface free energy, acid or base interactions) [504]. These methods may be especially required to quantify the effects of fibre pretreatment [503] used to improve fibre/matrix interaction. For instance, a higher contact angle for hemp fibre was reported when NaOH treated, which was beneficial in terms of thermal and wetting stability in the resulting thermoset composites [505]. Microbond tests with a polypropylene matrix revealed a better interface for hemp due to the presence of lignin in larger quantities. This has also been demonstrated by Graupner et al. [506] with jute fibres which are also highly lignified. These surface parameters are linked to the condition of retting and to the quality of the mechanical extraction of the fibres, but also depend on their own nature. Depending on the polymer used, it can therefore be taken into consideration in the choice of the reinforcing fibres. This is particularly true for hydrophobic polymers such as thermoplastic polyolefins. Although the interface can in this case be improved with a coupling agent such as maleic anhydride, the quality of the interface can be further improved by choosing a fibre rich in lignin. Although this parameter is not the first to be investigated, the researcher should have it in mind to optimise the quality of future composites. Premature breakages and low elongation are often considered to be the major defects of biocomposites. They can be related to the nature of the fibre and their morphology. The presence or absence of bundles is particularly important here, especially when they are stressed in transverse directions, as it is the case for example in an injected biocomposite [507] or for unidirectional reinforcements in the transverse direction [383]. The bundles constitute privileged areas of damage, their presence causes early breaks of the composite parts [367]. In this case, it is the fibre-fibre interface that is stressed and therefore the middle lamellae which

possess weak interfacial properties (about 7 times less than fibre-polymeric matrix). The elastic modulus of the middle lamellae measured by AFM is about 8 GPa [342]. This modulus is very close to the transverse modulus of a flax fibre also estimated to be 8 GPa [383]. Thus, biocomposites exhibit low mechanical properties in the transverse direction. Low transverse tensile strength is a major weakness of composites. The low value of the transverse tensile strength and the corresponding transverse failure strain are due to strain concentration in the matrix (or at the interface) around the fibres and the composite transverse tensile failure strain is often lower than that of the matrix. To improve the fibre individualisation during hackling, the middle lamella needs to be degraded. Coroller et al. [262] evidenced the crucial role of retting on injection-moulded biocomposite properties, especially on the strength values, and found high dependence on the degree of fibre individualisation. In general, at the fibre scale, the individualisation rate and the presence (or not) of bundles are essential parameters. Regardless of the microstructure of the future biocomposite, they largely impact its mechanical properties, especially in terms of failure and damage initiation. This point can be moderated according to the bundle's structure. In case of highly cohesive bundles such as of coir or jute, their division and breakage is not easy and polymer-fibre interface remains the main damage area. Nevertheless, at similar fibre volume fraction, the presence of large diameter bundles (with coir or jute for example) induces a reduction in the interfacial surface which is not in favour of good fibre-matrix stress transfer; for these reasons designer must prefer highly individualised reinforcements.

The mechanical performance of the reinforcing fibres greatly influences that of the associated biocomposites. In the case of a unidirectional composite, the longitudinal stiffness of the composites is directly driven by that of the fibres [508]. This is not the case for the stress at failure of the parts. Although the stress of the fibres has an impact on that of the composites, it is necessary to take into account other parameters. Thus, the individualisation of reinforcements, already underlined above, the quality of fibre/matrix interface or the length of the fibres and the presence of defects, have an important influence on the final strength value of the composite [262,509]. For unidirectional composites, it is possible to define an efficiency factor taking into account these different parameters. In the case of composites made from non-

wovens, depending on the porosity of the latter, the influencing parameters will not necessarily be the same [195]. If the performance level of the fibres is high, the state of division of the reinforcements remains a first order parameter and for materials with low densities, the quality of the interface between the fibre and the matrix is a very important point. The connection between the two components being affected by small surfaces bridges which are consequently highly stressed. When the densities are high and the porosity is limited, the structure of a non-woven composite can be similar to that of an injected part, except that its structure is homogeneous whatever the zone of the part in question. These properties are therefore relatively isotropic. In the case of an injected piece, things are different. The orientation mechanism of short fibres during injection moulding for reinforced thermoplastics is well-known in the case of glass fibre. The skin/core effect orientated to the flow direction in the skin layer and perpendicularly in the core layer has been demonstrated by many authors [510,511]. These orientation mechanisms can be predicted with numerical simulations [512]. Some authors [513] also show a significant increase of the thickness of the skin layer with the length of fibres because of the easier orientation for long fibres. In the case of reinforcement by short plant fibres (2 mm), the skin/core microstructure exhibits transitions between layers, but it is less noticeable than for glass fibres [367]. The mechanical properties of the composite vary depending on the fibre orientation and the skin and core layer thickness. In the skin layer, the fibres tend to be aligned in the direction of flow which leads to superior mechanical properties relative to the core where the fibres are more randomly oriented [367]. Graupner et al. [506] found on PLA/Lyocell moulded parts that the higher the fibre content is, the less the fibres were oriented in the flow direction. Indeed, by increasing the fibre content there are more interactions between the fibres, which leads to a decrease in the flow direction orientation [495]. Moreover, viscosity increases making flowing difficult and consequently lower fibre orientation. Thus, according to the final microstructure of the injected composite, mechanical properties can vary due to the important difference between skin and core orientation and longitudinal mechanical performances. The thickness of the skin area is governed by the melt viscosity, by injection parameters such as pressure and filling speed, by injection gate location, by the thickness of the part but also by the reinforcement structure [512]. Injected flax and jute biocomposites

microstructure was compared [514] and interestingly, for similar matrix and injection parameters, a thicker skin layer was highlighted for jute reinforcement, probably due to the reinforcement architecture. In the case of flax, the fibres are highly individualised, more flexible and more difficult to orient within the melt flow. Jute bundles have higher diameter and their high lignin rate make them more cohesive; this specific structure eases their orientation and is in favour of aligned reinforcement, leading to higher longitudinal composite performances. Figure 35 shows a comparison of a cross section of PP-flax and PP-jute.

Figure 35

By working on different varieties of flax, Haag et al. [515] have shown that the bundles fineness was a parameter strongly linked to composite properties; nevertheless, the impact of this individualisation is not the same according to the used processing method.

Thus, although fibre parameters that have a notable influence at the composite scale can be identified, nevertheless their degree of influence can vary according to the kind of composite. Degree of individualisation is a crucial parameter, having a strong influence on both strength and interfacial properties; it must be favoured to optimise composite properties. Fibre mechanical properties are also key, and generally, higher fibre mechanical performance lead to better the composite mechanical properties; this is especially true for unidirectional composites, but also for non-woven composites. Finally, for injection-moulded composites, the microstructure of the parts is an essential parameter. It is largely influenced by the ability of the reinforcement to be oriented within the polymer flow. In this way the architecture of the reinforcement and its stiffness is a key parameter which can be more important than the fibre mechanical properties.

3.4.4. Plant fibres hierarchy for use of composite reinforcement

The last part of this review aims to propose a classification of plant fibres that can be used as composite reinforcements. As we have just mentioned, it is difficult to propose an elementary classification given the structure of the materials and the stresses on the composite materials which can be very different according to their nature and their applications. We propose to present three cases: (i) unidirectional composites with long fibres, (ii) injection-moulded short fibre composites, and finally (iii) composites made from nonwovens of plant fibres. For each case, according to the most influential parameters identified in the previous section, but also taking into account the availability and cost of the reinforcements, we will propose the most relevant fibres.

Figure 36

Figure 36 proposes a synthetic view of both reinforcement and composite architecture diversity. It graphically shows the large panel of fibre properties available, particularly stiffness and morphology, which largely depends on the nature of the reinforcement (whether it is a elementary fibre or bundle). As explained previously, according to the biochemical composition of the plant cell walls and middle lamellas linking the elementary fibres, the majority of the elementary fibres or bundles can be present within the composite, even after a process cycle [262,514]. Of course, the mechanical properties of the fibre elements are also strongly impacted by the morphology of these latters and especially if they are elementary fibres or bundles being an assembly of several elementary cells with interfacial bonds.

In the case of unidirectional composites, the mechanical performance of the reinforcements is particularly important as they directly affect the stiffness and the strength of the materials. Moreover, the level of division of the fibres and the availability of long elementary fibres is also a very important point. Furthermore, the elaboration of the unidirectional fabric, and especially the potential twisting of the yarn is a key point parameter, limiting fibre impregnation, favouring the presence of porosities and consequently limiting composite performance [516,517]. The

selection criteria generally used for unidirectional design are the stiffness of the reinforcements, the length of the elementary fibres and their diameters.

Figure 37 synthesises literature data on Young's modulus and strength at break for unidirectional plant fibre composites. These composites were manufactured with an epoxy matrix and a large diversity of plant fibres. Interestingly, one can notice that the Young's modulus is moderately affected by the morphology of the fibre's elements; the best values are obtained for flax due to the high individualisation rate of hackled flax but also due to the good mechanical performance of isolated fibres. Nevertheless, large values can also be obtained with jute, when suitable reinforcement can be used. Of course, due to lower mechanical properties of jute cell walls a shift in the gradient of the stiffness-volume fraction curve is noticed. Nonetheless, these different values come from different references, showing the potential reproducibility of jute fibre composites properties. The important takeaway is that here, the stiffness of unidirectional plant fibre composites is mainly governed by the cell wall stiffness (Figure 7) and not by the elementary fibre length (Table 1). Nevertheless, the aspect ratio does contribute, especially in a detrimental manner, as noticeable for high bundle diameter fibres such as coir.

Figure 37

Things are a little different for strength. Unidirectional flax composites exhibit higher values, particularly as the considered batch of fibres was hackled and thereby exhibitting high fibre division. Moreover, these fibres exhibit the best elementary fibre strength at break (Figure 7), as well as large elementary fibre length, which is of utmost importance for stress-transfer between fibre and matrix. The composite strength at break is lower for hemp, jute, kenaf and coir fibres. These fibres, due to their important lignin content, are generally assembled in cohesive bundles having larger diameters. This morphology induces lower reinforcement aspect ratio which is a

limiting factor for stress transfer and high strength levels. We showed in a previous work that the bundles are also preferential areas for breakage initiation [367].

Thus, depending of the considered mechanical properties, modulus or strength, the choice of the reinforcement fibres can be different, but in general, best properties are obtained with the reinforcements having better elementary fibre mechanical properties, fibre length and division. Young's modulus is more dependent on fibres mechanical properties, while for strength, the individualisation and aspect ratio are also key elements.

Applications for unidirectional composites typically involve high value-added sectors such as naval or aeronautic. Although important, the cost of reinforcements is not always a decisive criterion, but must be considered alongside the environmental impact resulting from the fibre's production and extraction.

Short-fibre injection-moulded composites are mainly reserved for applications with large volumes due to the high cost of production equipment. These markets mainly concern the automotive sector, and the cost and availability of materials make sense here. As mentioned, the structure of the reinforcements, which plays an important role on the microstructure of the parts, must be taken into account in the choice of reinforcements. The mechanical properties of the fibres must also be taken into consideration. For these reasons, we have chosen to consider in our classification the mechanical performances of the reinforcements, their lignin ratio, the aspect ratio and diameter of the objects. For instance, a small diameter penalises the orientation capacity, while and a large diameter penalises the interfacial surface. We also integrate their cost and availability in this analysis.

Figure 38

Figure 38 shows the main properties of a panel of plant fibres and the Young's modulus of the associated composites. Reinforcement loading is the same (30%-wt) as well as the matrix (Poly-(propylene) PPC 10642 from Total Petrochemical with 3% of maleic anhydrid grafted PP

(Orevac 100 from Total Petrochemical)). Moreover, compounding and injection moulding were performed with the same equipments. For each parameter, except composite stiffness, values are presented relative to the higher one.

As discussed in 3.4.3 section, the composite stiffness classification is not directly linked to the Young's modulus of the fibre. Indeed, flax and hemp, which have the best fibre stiffness exhibit a composite modulus lower than that of jute composites. As explained before, the orientation ability of the bundles has a strong influence and hemp or flax, mainly due to their high aspect ratio and low lignin content have softer and less cohesive bundles, limiting their flow orientation. Nevertheless, these considerations have some limits. For example, coir, which has a large diameter, a low aspect ratio and a high lignin content, exhibits a poor composite reinforcement ability. The large diameter of coir fibre bundles as well as their porous structure are, in this case, limiting and induce a reduced interfacial surface between matrix and bundles within the composite. Thus a compromise must be found, based on fibre performance and morphology and structure. Here, jute fibres are a good example, having limited mechanical performance, but an ideal structure for a suitable orientation within an injected part (Fig. 35). Injection-moulded composites, considering the high cost of tooling, are generally carried produced at large scales (at least a few hundred thousand pieces). Thus, the necessary volumes are important and this must be taken into account in the availability of the plant fibre resource. The cost of reinforcement is often a decisive factor in the choice of the latter, especially in very competitive sectors such as the automobile one. For this reason, these two parameters also appear in Fig. 38. It can be seen that the high cost of flax fibres, as well as their relatively low availability, can be a constraint on their incorporation into parts for high volume markets. On the other hand, once again jute satisfactorily fulfils these two criteria. Wood, which is very abundant and inexpensive, can also be seen as an alternative resource, especially when it is available in the form of individual Woodforce© fibres that exhibit aspect ratios and interesting performances within composites. Finally, the local aspect of the resource must be taken into account in order to combine performance and low impact on the environment. Thus the injected composites produced in Asia will be able to favour jute, while those made in Europe will favour hemp or the flax, whereas the wood can be chosen in North America.

Finally, the case of low density biocomposites made from nonwovens of plant fibres can be studied. Figure 39 shows their specific structure, highlights the strong dependence of their acoustic and mechanical properties to their density and finally presents a list of their main influencing parameters.

Figure 39

These lightweight materials are mainly used in the automotive and construction sectors. They are therefore also important markets in terms of volume. If the price of the fibres is large it must be normalised here because in the case of flax, these materials are generally made from co-products such as tows. For this reason, this economic parameter has not been taken into account here as the cost of flax tows may be of the same order as that of hemp, jute or sisal tows.

Non-wovens are shaped by compression moulding and, according to process parameters, the densities of the final parts can vary considerably, depending on the desired characteristics. Consequently, the nature of the fibres plays a particularly important role on the performance of these materials. If acoustics are favoured, the densities will be low whereas they will be higher if the part must have a mechanical function. In view of an acoustic application, the porosities of the material will play a role but those present in the reinforcements also. It will then be pertinent to favour fibres having large lumens such as those of jute or sisal. Their apparent morphology will also be a criterion of choice; indeed, the stiffness and maximum stress performances of these composites are largely influenced by the interfacial surface which is conditioned by the degree of individualisation of the reinforcement and the microstructure or the density of the stack. The higher the interfacial surface area, the greater the number of stress transfer zones from one reinforcing fibre to the other. The relevant parameters identified here are thus both the degree of individualisation and the diameter of the fibres, as well as their lengths which can influence the slippage between fibres.

The quality of the interface is also paramount, especially for parts with very low densities for which the structure of the material is very dependent on the connections between fibres and matrix. Graupner et al. [525] showed that lignin could significantly improve this interface by acting as an adhesion promoter. Thus, depending on the nature of the fibres used, the quality of the interface may vary, and reinforcements of jute or hemp may then present an additional attraction with respect to flax.

Finally, even if it is not preponderant here, the mechanical performance and especially the specific fibre stiffness of the reinforcements also influences that of the composite and must be taken into account; especially when high density materials are considered.

Through these three different examples we were able to define the relevant parameters to be considered when selecting plant fibres to achieve the best composite performance. These factors are based on the authors' experience (and that of the wider biocomposites community), but the designer must always have a critical eye on the reinforcements used and adapt their decisions based on the specific needs. The matter is complex to want to generalise into point-by-point conclusions. We encourage questioning of the principal parameters depending on the nature of the polymers used, the process conditions or the geometry of the tools, which are paramount parameters for obtaining high-performance composites.

4. Conclusion

Through this critical review, we have proposed a classification for the different families of plant fibres that offer potential to reinforce composite materials. Their industrial use demands reproducibility and consistency in performance of the plant fibres, near-perfect knowledge of the structure and properties of the fibres, as well as the definition of a common language between scientific communities. Different aspects were described, especially the particularities of the fibres in terms of their structure and properties, as well as the impact of selected extraction and treatment processes on the environment and

their potential as composite reinforcements. We highlighted and discussed important parameters that enable selection of the best-suited vegetable fibres according to their use and the envisaged applications. This review was divided into two main parts. In the first, we proposed classification of a panel of plant fibres that can be used as reinforcements in composite materials. The technical-economic study focused on the prices of raw materials and their availability. The field of plant fibres comprises different markets with distinct characteristics. In terms of volume, it is dominated by wood, which can provide a very abundant biomass, which is inexpensive but with often only moderate performance. Cotton also occupies a large part of the volumes available, and its fibres have high (and useful) aspect ratios, but its mechanical properties are not ideal for composite reinforcements. Finally, fibres with the greatest reinforcement potential are available at widely varying levels, ranging from about 60,000 tonnes for hemp to over 3 million tonnes for jute. Their respective availability varies according to the geographical location on the planet, which is of interest for the environment, since each industrial centre can locate available resources locally. These different reinforcements possess specific mechanical performances that are strongly related to the biochemical composition and structuring of their cell walls, as well as to their morphology. The size of their lumen, their cellulose content and their microfibrillar angle are important criteria governing the apparent stiffness of the fibre reinforcements. These intrinsic properties of the walls are partly related to the location of the fibres in the plants. Fibres that are real supporting elements in the plant stem, as is the case for flax and hemp, exhibit strong mechanical performance. In contrast, fibres that have a role of protection against impact/shock or moisture, as is the case for coir, or of protection of the vascular bundles of the leaves, as is the case for sisal, will naturally have a lower performance. In addition to this role, their growth behaviour, influenced by and the external stresses undergone, the conditions during growth, the cultural practices employed, also dictate the quality of their performance. Furthermore, the quality of the reinforcements is strongly linked to retting and extraction conditions. It is necessary to control the phase of retting so as not to degrade the walls but also to promote the ability of the fibres to individualise without

damaging them. Water retting, which is still present for certain types of production, is to be avoided for environmental reasons and alternative techniques such as enzymatic retting or steam emission are not widely used because of their cost and difficulty in industrialisation. Finally, our work stressed the importance of the mode of extraction of the fibres; if poorly controlled, it can increase the amount of defects such as kink bands which will be detrimental to the final performance of the composites.

In the second part of the manuscript, we were interested in how to best characterise plant reinforcements for applications in composite materials. First, we have focused on the differences in views and experimental techniques employed depending on whether the experimenter or the designer is an engineer or a biologist. Unlike the engineer, a specialist of the plant cell walls focuses on the differences in terms of structuring of these materials. We have chosen to detail the differences in structure that can coexist, sometimes even within the same fibre. This is the case, for example, for the Gn and G layers of wood and flax, which can induce considerable intra-fibre contrasts but also strong similarities between two opposing *a priori* fibres. Next, we asked ourselves the question of the relevant scale of characterisation, always with the objective of measuring mechanical properties relevant to the engineer or the designer of composite materials. By this synthesis, we showed that most mechanical parameters were accessible using characterisations at the scale of the stem, the bundles, the elementary fibre or even the plant cell wall. These data may be obtained directly or by inverse methods. Nevertheless, particular attention must be paid to possible discrepancies in terms of measurements for the same property made at different scales. This case is particularly obvious for the measurements of stiffness which differs radically according to whether one considers local cell wall stiffness, influenced by the transverse component and measured in AFM or nanoindentation, or an apparent and overall modulus of the fibre obtained by tensile on elementary fibre. These mechanical considerations are also valid for measurements of microfibrillar angles or the determination of the biochemical compositions of the walls. For these two parameters, different methods, sometimes giving very different results, exist

and the comparison of the data from the literature must be done with care to avoid any hasty conclusions.

Finally, this section concludes with an important part dedicated to the choice of fibres for the best possible use as polymer reinforcements. We have come back to the proven importance of retting on fibre individualisation and surface quality. This primordial step must be mastered and over-retting, which penalises the mechanical performances of fibres and composites, must be avoided. The retting can have direct consequences on the individualisation of the fibres and on their adhesion with the polymer matrices. The nature of the walls also plays an important role; lignin being considered as a promoter of adhesion. A hierarchy in terms of mechanical performances, diameters, aspect ratios or lengths exists among the different species of fibres; it can also be found at the composite level. If the correlation between the stiffness of the fibres and the composite is evident for unidirectional long fibres, this is less clear for the strength of these materials, largely influenced by the individualisation of the reinforcements. In the case of injection-moulded composites, the microstructure and the orientation of the reinforcements are preponderant, more than the mechanical performances of the fibres, as we have shown by taking the case of flax and jute. Cost and availability are also factors to consider because of the large volumes needed to justify large equipment installation costs. These economic considerations also exist for compression-moulded non-woven composites, which also concern mass markets. In this case, the mechanical performances of the fibres are important but, depending on the desired densities, the division, the length or the quality of the interface between the fibres and the matrix are key points, in particular for light and porous final parts for which the points of attachment with the matrix are limited.

Thus, through in this review, we have shown that there is a wide diversity of plant cell walls based on their apparent performances in a panel of studied composites. Their behavior during processing may differ drastically from one to another and we give a comprehensive review of the origins of those contrasts. First of all, we review key criteria that biocomposite engineers and scientists must consider to select or understand behaviour at the source of the plant fibre. Potentiality and limits of plant fibres are strongly

linked to their location within the plant and consequently to their structure and biochemical composition. The same cell wall could be seen in different ways according to the culture, the knowledge, the sensibility as well as the investigation methods. The differences in the fibres have to be taken into account as part of the composite design step in an environmental and societal approach. Moreover, dedicated growing and suitable mechanisation should be used to obtain the composite materials as good as possible. Industrially speaking, composite manufacturers want to obtain plant fibres in large quantities and with consistent properties, even at the cost of losing (some) performance. This point must be taken into account even if properties are homogenised within a composite. Finally, plant fibres applications are mainly for the textile industry and most characterisation tools are adapted to this sector; with the development of composite markets, new pertinent tools have to be developed.

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Tables caption

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Table

Table 1. Morphological properties of elementary lignocellulosic fibres

	Length (mm)	Diameter (µm)	MFA (°)	Density [g/cm³]	Reference
Musa textilis (Abaca)	2-12	6-53	5-17	1.5	**Reference**
Stipa tenacissima (Alfa)	2-5	5-10	-	1.4	[42–45]
Bambusoideae (Bamboo)	0.5-5	5-40	8-10.7	1.15-1.41	[46,47]
Cocos nucifera (Coir)	0.28-1.1	5.6-19.5	30-49	1.15-1.3	[48–51]
Gossypium sp. (Cotton)	10-60	12-38	20-30	1.5-1.6	[52–55]
Linum Usitatissimum L. (Flax)	6-80	12.4-23.9	8.3-11	1.53-1.54	[56,57]
Cannabis Sativa (Hemp)	5-55	10.9-42.0	11	1.4-1.6	[20,22,27,58–62]
Corchorus capsularis (Jute)	1-6	15-35	7-12	1.38-1.40	[21,63–71]
Ceiba pentandra (Kapok)	7-35	8-35	5	1.3	[56,57,72–77]
Hibiscus cannabinus (Kenaf)	2.1-2.7	2.1-36	9-15	1.45	[78–82]
Boehmeria nivea (Ramie)	120-150	10-50	7.5	1.5	[83–87]
Agave sisalana (Sisal)	0.5-8	10-20	20	1.45	[88,89]
Wood (different species)	1.0-8	10-60	5-40	1.44-1.50	[78,90–92]
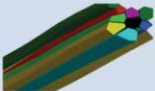
Table 2. Mechanical properties of lignocellulosic fibres elements (elementary fibres or bundles)

	Elementary fibre or bundle	Diameter (μm)	Young's Modulus (GPa)	Strength at break (MPa)	Strain at break (%)	Reference
Musa textilis (Abaca)	Bundle	179-230	17.1-18.4	755-798	8.8-6.2	[98,99]
Stipa tenacissima (Alfa)	Elementary and bundle	24.3	31.0-71.0	679-1480	2.4-2.8	[47,100]
Bambusoideae (Bamboo)	Elementary	13.4	32.0-43.7	1200-1610	3.8-5.8	[48,49]
Cocos nucifera (Coir)	Bundle	100-460	3.39-17.3	131-343	3.7-44.7	[52,53,75,101]
Gossypium sp. (Cotton)	Elementary	No bundle	5.5-13.0	287-800	3-10	[56,102]
Linum Usitatissimum L. (Flax)	Elementary	12.4-23.9	37.2-75.1	595-1510	1.6-3.6	[20,22,58,59,103]
Cannabis Sativa (Hemp)	Elementary / Bundle	10.9-42.0	14.4-44.5	285-889	0.8-3.3	[21,66–68,70,104,69,105]
Corchorus capsularis (Jute)	Bundle	60-110	10-31.2	114-629	1.5-1.8	[56,77,106,107]
Ceiba pentandra (Kapok)	Elementary	23.6	1.7-4.0	45-93	1.2-4.0	[79,80]
Hibiscus cannabinus (Kenaf)	Elementary	13.3	19	983	4.5	[108]
Boehmeria nivea (Ramie)	Elementary	34-50	24.5-65	560-900	1.2-2.5	[57,89,109]
Agave sisalana (Sisal)	Bundle	25-252	9.0-25.0	347-577	2.3-5.45	[90,110,111,69]
Wood (different species)	Elementary	15.5-22.6	15.4-27.5	553-1300	3-7	[112–116]

Table 3. Biochemical composition of lignocellulosic fibres

	Cellulose	Hemicellulose	Lignin	Pectin	Fat and Wax	Reference
Musa textilis (Abaca)	60.8-68.0	17.5-21	5-15.1	<1	<1	[72,117,118]
Stipa tenacissima (Alfa)	43.9-48.0	25.7-38.5	14.9-23	1	1-3	[46,47,100,119]
Bambusoideae (Bamboo)	36.1-54.6	11.4-16.6	20.5-28.5	<1	1-4	[120–122]
Cocos nucifera (Coir)	32.0-43.4	0.3	40-45.8	3	0-6	[52,76]
Gossypium sp. (Cotton)	82.7-98.0	4.0-5.7	0.7	4	2-3	[102,123]
Linum Usitatissimum L. (Flax)	60-85	14.0-20.6	1-3	1.8-15.0	1-6	[124–128]
Cannabis Sativa (Hemp)	55-90	12	2-5	3	1.7	[21,63,129–134]
Corchorus capsularis (Jute)	58.0-71.5	13.6-24.0	11.8-16	2	<1	[106,135]
Ceiba pentandra (Kapok)	13-35	23-32	13-21	7-23	<1	[79,80]
Hibiscus cannabinus (Kenaf)	52.0-61.2	18.5-29.7	12.9-16.1	3-5	<1	[83–85]
Boehmeria nivea (Ramie)	61. 8-76.2	5.3-16.7	0.6-9.1	0.3	<1	[136,137]
Agave sisalana (Sisal)	52.8-65	19.3	11.1-13.5	10-14	<1	[138,139]
Wood (different species)	38-45	19-39	22-34	0.4-5	<1	[93,140,141]

Table 4. Synthesis of mechanical data potentially obtained through multi scale mechanical characterization. Composite inverse method is added to complete this summary.

Testing mode		Data
	Cell wall testing; Nanoindentation / AFM	E_{FLnano}, E_{FTnano}, H_{nano}
	Single fibre tensile testing	Stress-Strain curve, E_{FL}^{+}, σ_{FL}^{+}, ε_{FL}^{+}
	Bundle tensile testing	E_{FL}, τ_{ML}
	Stem bending testing	E_{FL}, ε_{FL}^{-}, σ_{FL}^{-}
	Composite scale (inverse method)	$\left[E_{FT}, E_{FL}, G_{FLT}, \nu_{FLT} \right]$

Table 5. Comparison between tensile, nanoindentation and AFM mapping longitudinal stiffness for various fibres.

Sample	Elementary fibre tensile modulus (GPa)	Nanoindentation modulus (GPa)	AFM mapping modulus (GPA)	Reference
Eden flax	68.9 ± 24.6	20.4 ± 1.1	21.3 ± 2.2	[164,342]
Bamboo	43.6 ± 0.6	21.3 ± 1.7	21.3 ± 2.9	[48,397,421]
Tension wood	18-40	14-20	11	[399,410]

Figure

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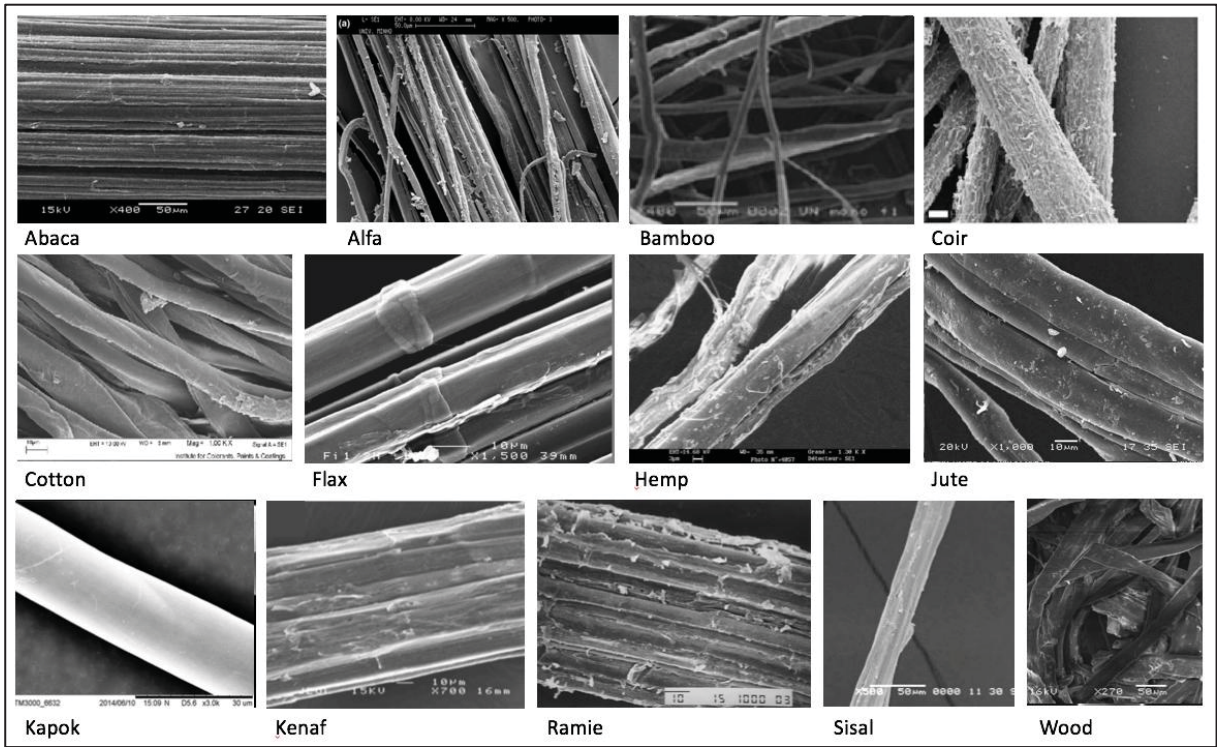
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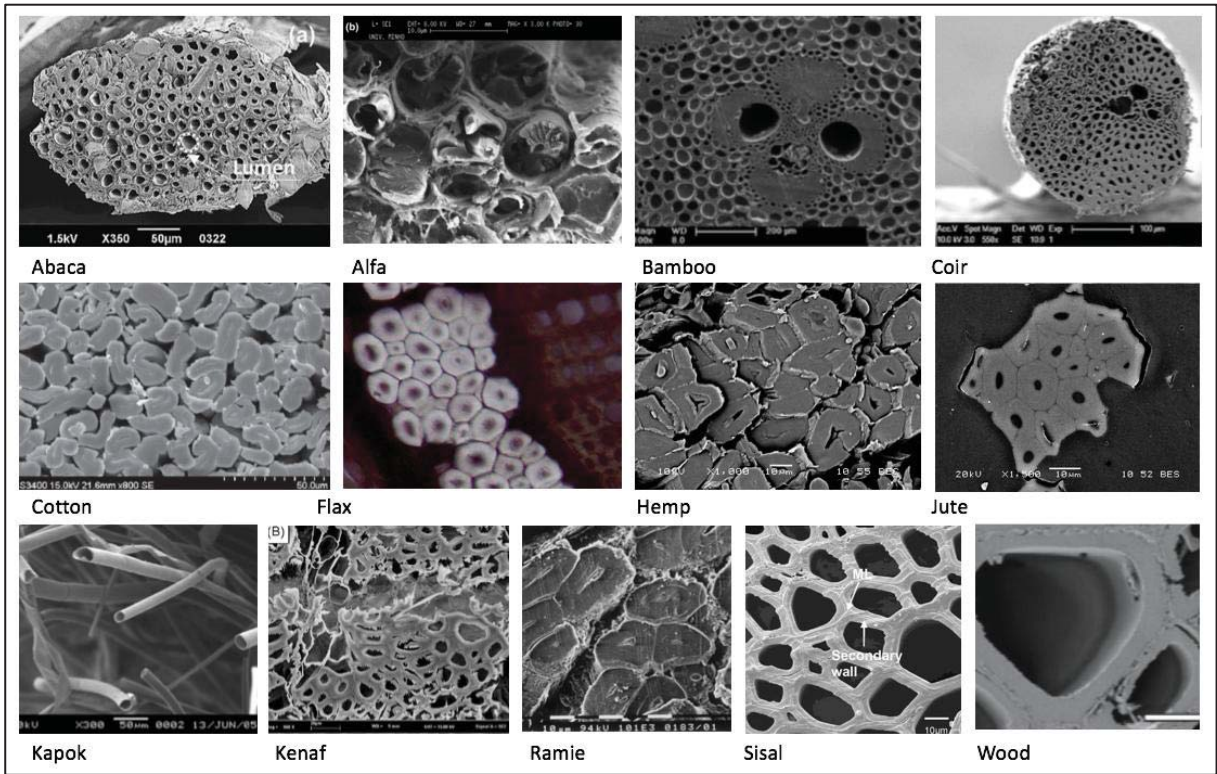
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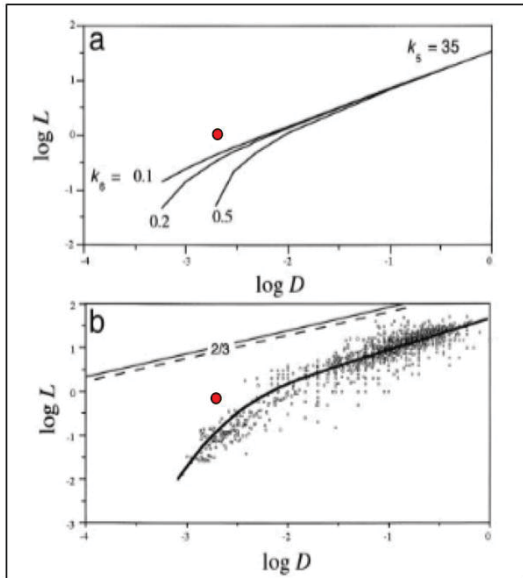
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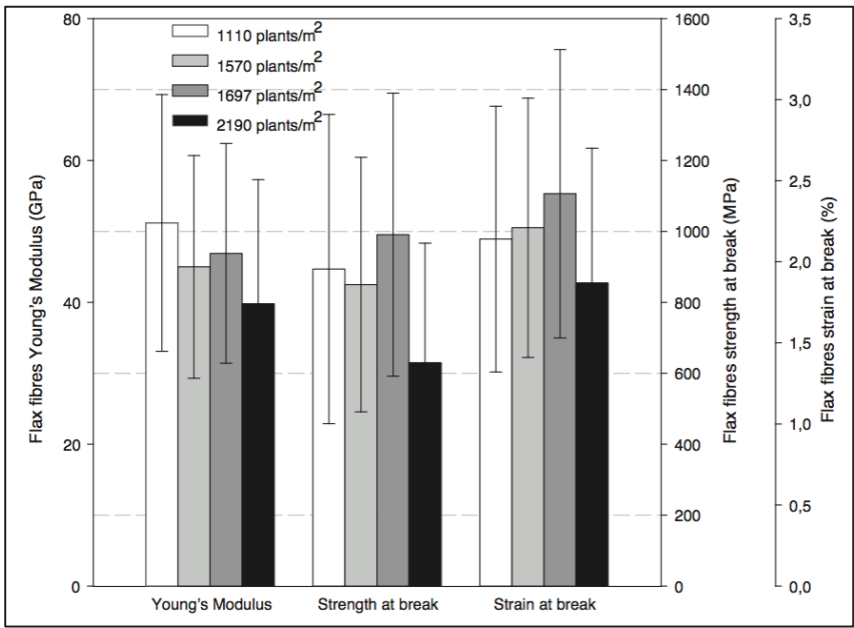
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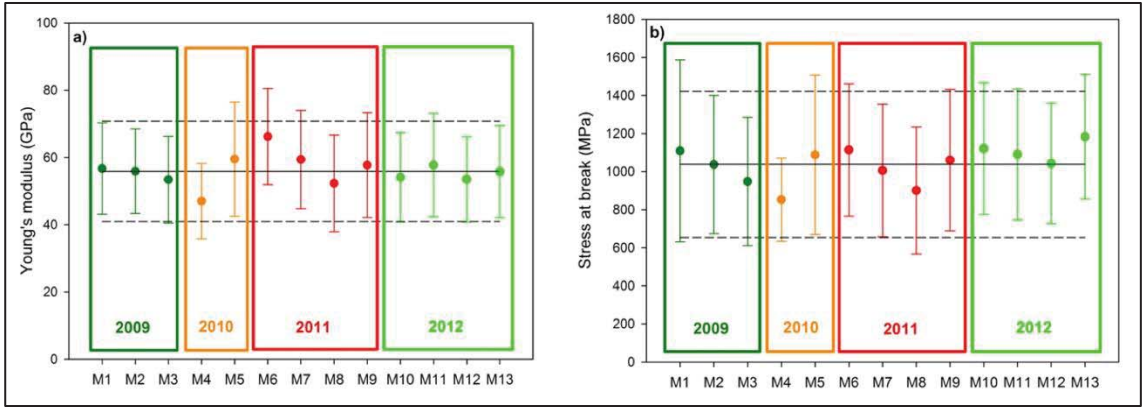
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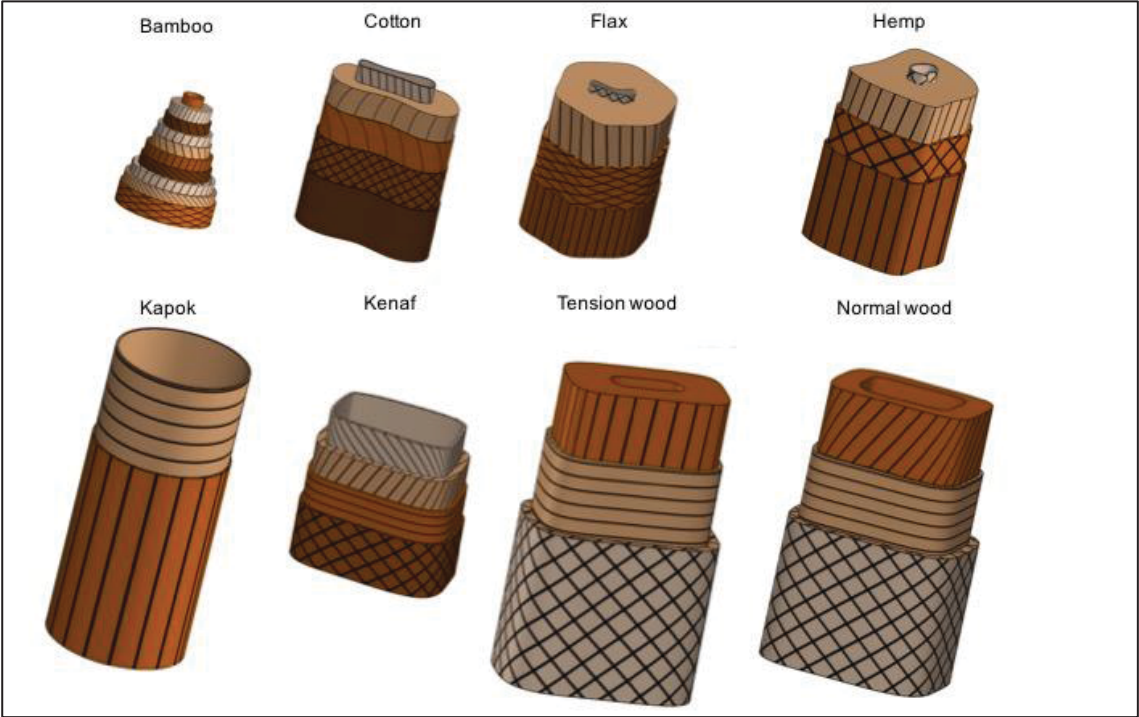
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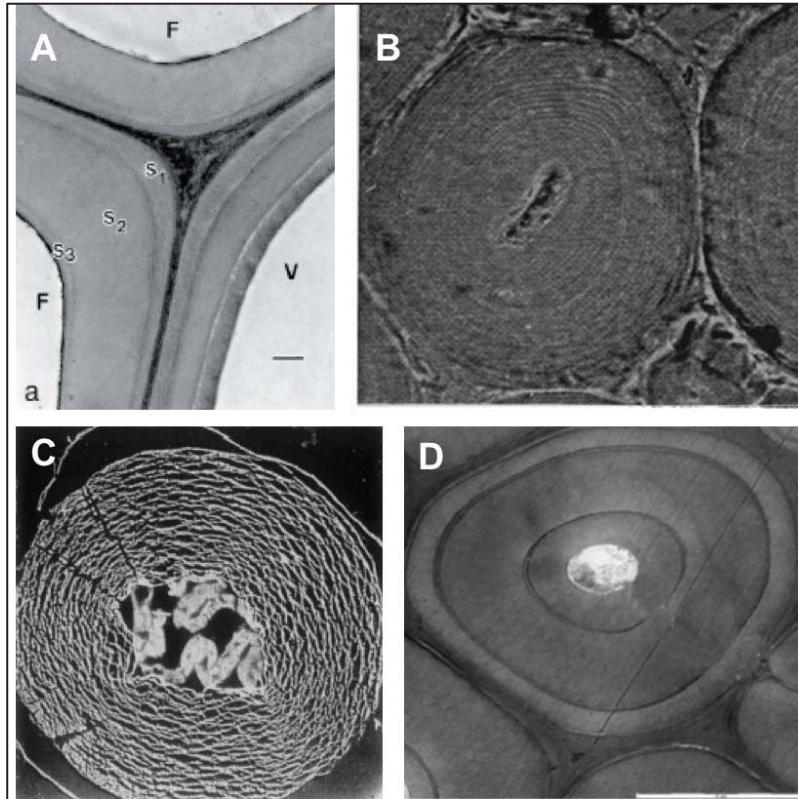
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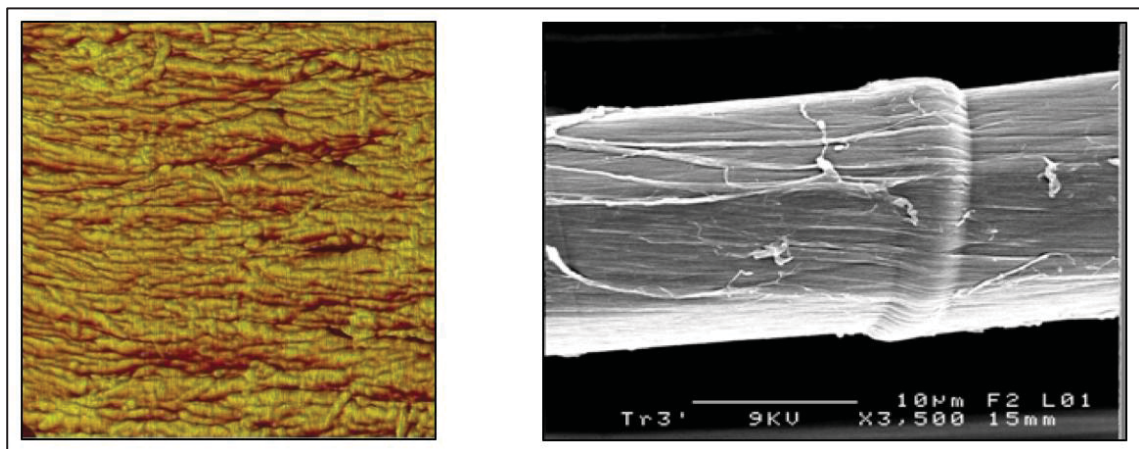
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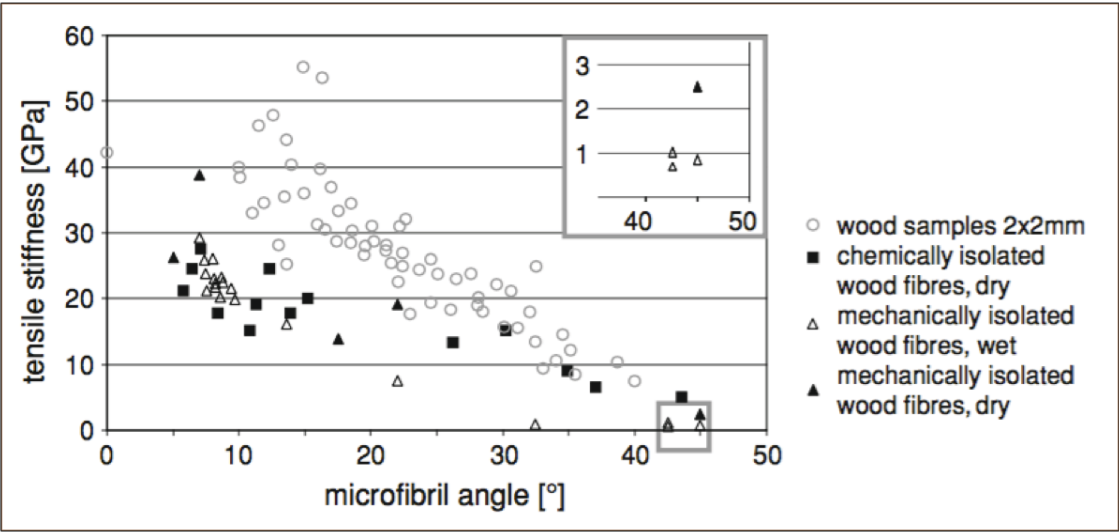
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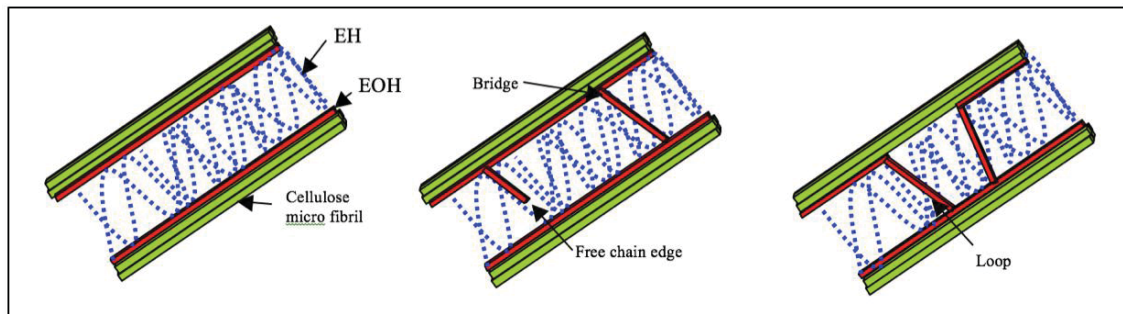
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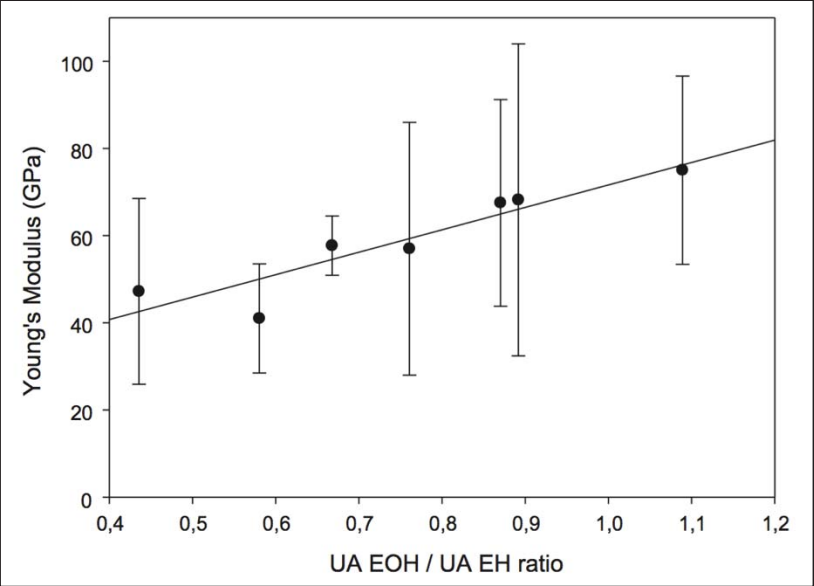
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(a)

(b)
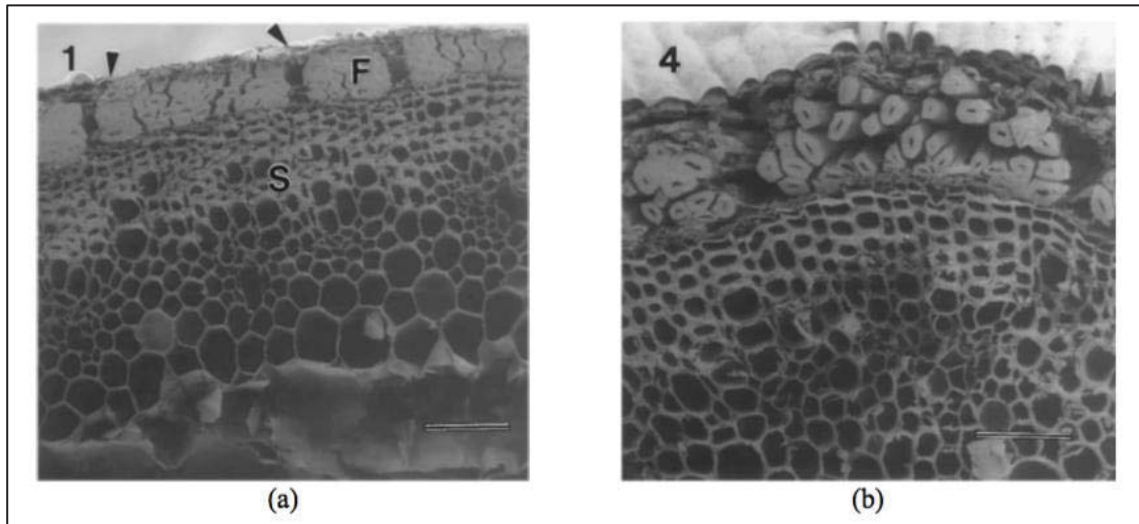
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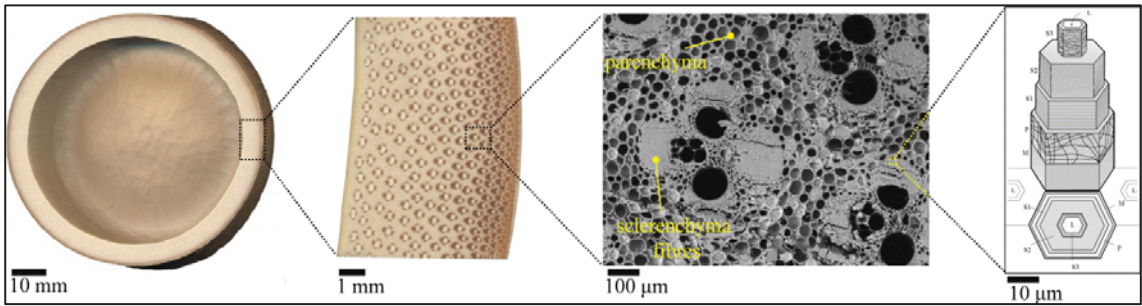
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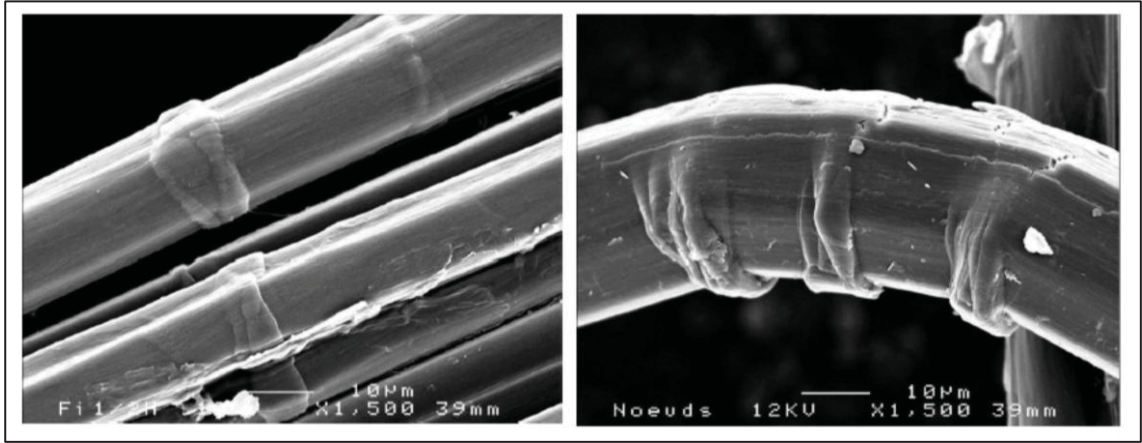
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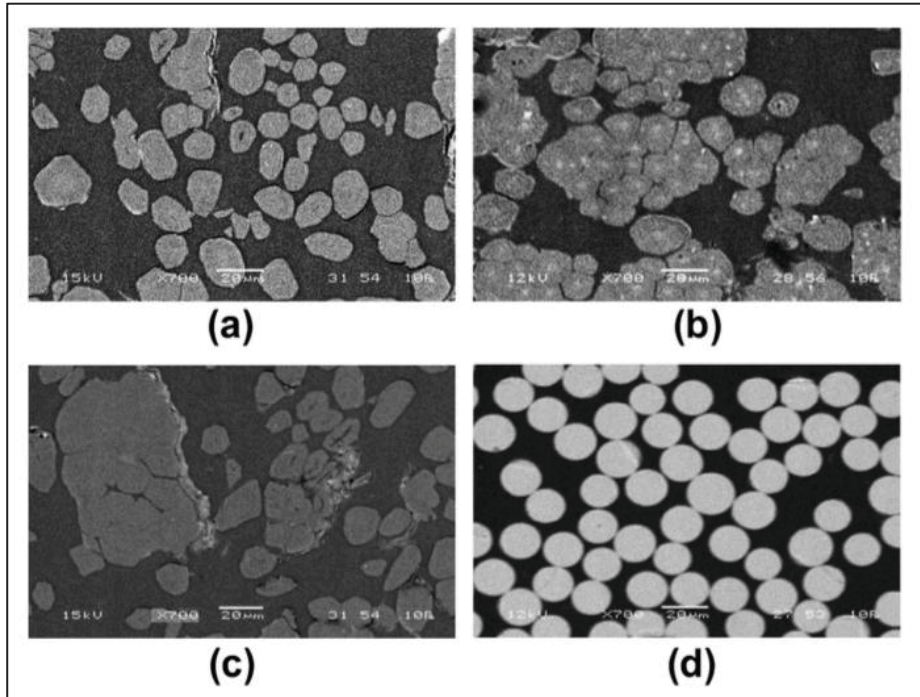
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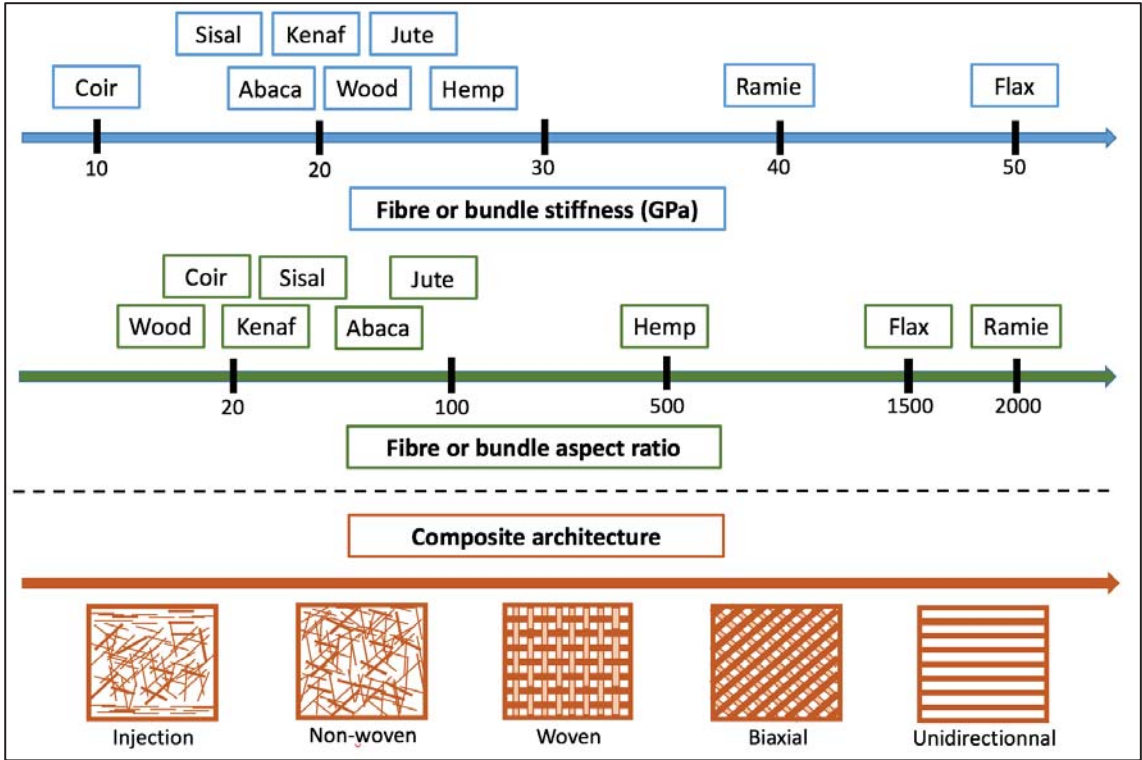**Figure 34.** Impact of retting on fibres and composite properties.

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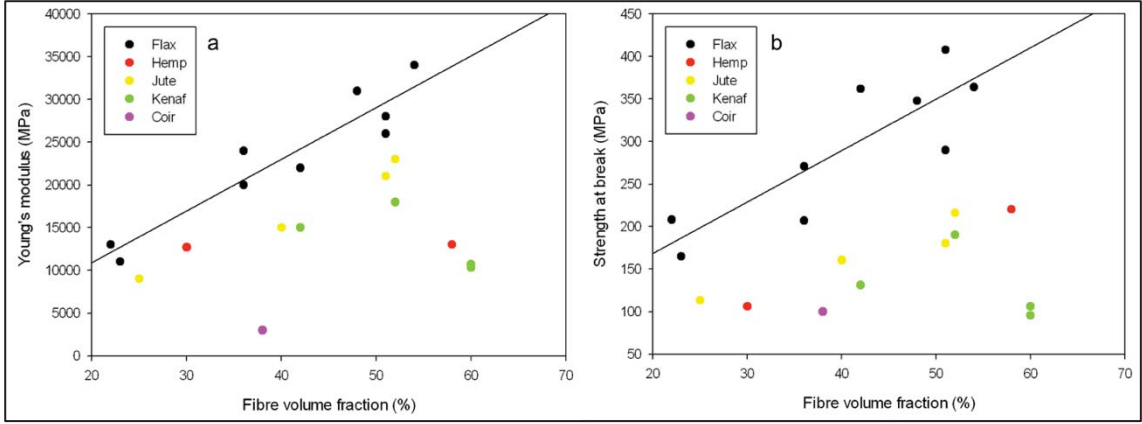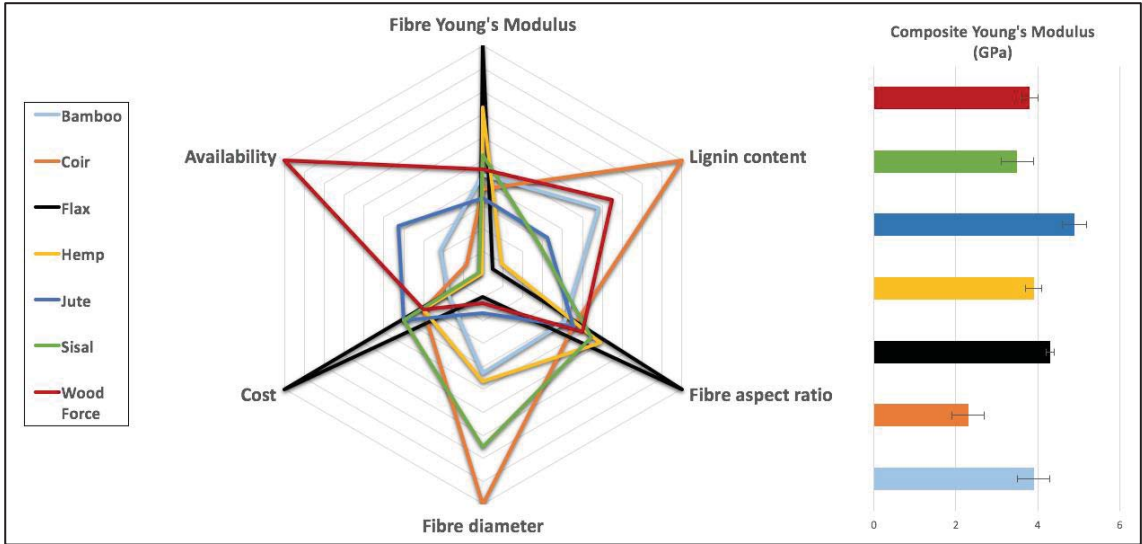
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