ANALYSIS OF SHEAR PROPERTIES OF FLAX FIBRES- INFLUENCE OF DRYING PROCESS

A. Le Duigou[1]*, C.Baley[1], A. Bourmaud[1] and P. Davies[2]
[1] LIMATB Laboratoire d'ingénierie des Matériaux de Bretagne, Equipe Polymères et Composites, Rue de Saint Maudé BP 92116, 56321 Lorient Cedex, [2]IFREMER Materials and Structure group, Brest Centre, BP 70, 29280 Plouzané
* Corresponding author (Antoine.le-duigou@univ-ubs.fr)

Keywords *:Flax fibres, mechanical analysis*

1 Introduction

Vegetal fibres can be described as a stack of composite plies reinforced by cellulose fibrils with particular orientation [1]. The most external layer consist of a primary wall while secondary whose structure is divided in 3 layers (S1, S2 and S3) represent around 80% of the fibre cross section. In secondary wall, cellulose fibrils are embedded in amorphous polysaccharides matrix mainly composed of pectins [2], hemicelluloses [3] and low amount of lignin. This complex hierarchical architecture involves particular mechanical behavior [4].
Flax fibres are more and more studied. Indeed their rigidity is as high as those of glass fibres [4, 5] while they have low environmental impact [6]. Their mechanical properties depend on cellulose content in S2 layer, microfibrillar angle, cell-wall shape and thickness, shearing properties of cellulose fibrils/polysaccharide matrix interface [7, 8]
Once used as reinforcement of thermoplastic composites, vegetal fibres undergo high temperature which alter their water content. The purpose of this works is to evaluate the influence of drying on tensile behaviour and shearing properties of S2 cell-wall.

2 Material and Method

2.1 Material

Flax fibres from ARIANE variety are selected. They are cultivated in Normandy (France) and are dew retted, scutched and hackled. This is the same batch as reference [4].

2.2 Tensile tests

Tensile tests on single fibres were carried out at a controlled temperature (23°C) and relative humidity (48%). Due to the short fibre length (about 20–30 mm), a gauge length of 10 mm was chosen. The fibre was clamped on a universal MTS type tensile testing machine equipped with a 2 N capacity load cell and loaded at a constant crosshead displacement rate of 1 mm/min up to rupture. The determination of the mechanical properties was made in accordance with the NFT 25-704 standard which takes into account the compliance of the loading frame. For each kind of fibre, at least 50 fibres were tested. Before tensile test, the diameter of every fibre is measured with an optical microscope. The diameter taken into account is an average value from three points obtained along the fibre.

2.2 Drying

Fibres are dried 24h at 105°C. This temperature is commonly used to determine bonded water content within wood cell wall [9]. The drying device is placed close to the tensile machine and tensile test requires 2 minutes. Previous work [10] has shown the evolution of water uptake after drying flax fibres Thus it is possible to know the water content inside flax fibres.

2.3 Thermogravimetric analysis

In order to quantify the influence of drying on flax fibres, a TGA analysis was carried out. Experiment was performed using a Mettler Toledo TGA/DSC 1

apparatus. The analysis was done according to the following protocol :

- Ramp from 25°C to 105°C at 20°C/min
- Isothermal at 105°C during 14h

Around 100 mg of fibre was used. Weight changes versus time were recorded.

3 Results and discussion

3.1 Thermogravimetric analysis

Figure 1 shows the mass loss for Ariane flax fibres during the thermal cycle (14h at 105°C).

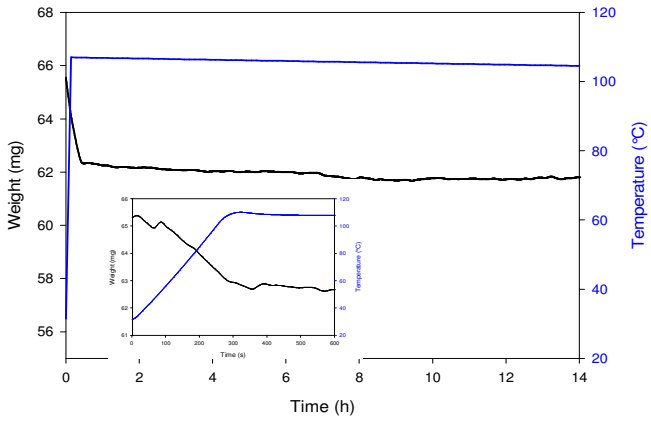

Fig. 1 Thermogravimetric analysis of flax fibres kept at 105°C during 14H. Insertion shows a zoom of the beginning of the thermal curve

Most of mass loss occurs at the beginning of the heating ramp during the first minutes. This mass reduction around 5.1 % can be attributed to the water loss. This value is below the water content measured on this variety (6.4%) but it can however correspond to water located at the surface and associated with pectins coming from residual middle lamellae.
Then loss of water continues along the 14h isotherm cycle to reach a total amount of 5.9%. This trend is certainly due to partial evacuation of internal cell wall bonded water.

3.2 Influence of water loss on mechanical behaviour and properties

Figure 2 presents the common tensile behavior of raw and dried flax fibres.

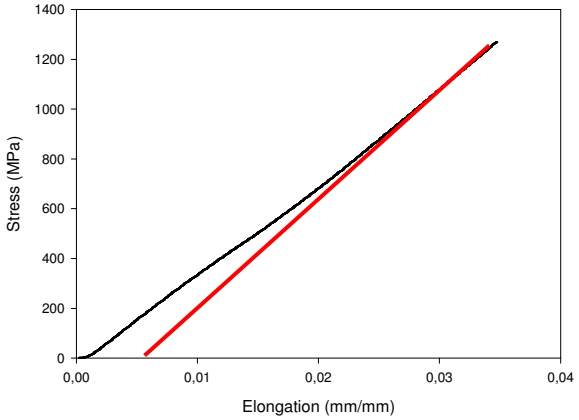

Fig. 2 Typical tensile behaviour for raw and dried flax fibre

Particular bevahiour is observed with the appearance of a yield point corresponding to loss of linearity due to hierarchical structure of natural fibre. Data from literature show that similar behaviour is observed for synthetic fibre such as PET or PA [11].

Mean mechanical properties are gathered in Table 1. Young's modulus and tensile strength are function of fibre diameter [4, 12], therefore mechanical properties are shown for diameter range (20-22.5 µm and 22.5-25 µm) which correspond to the mean diameter.

Table 1 Analysis of the influence of drying on tensile properties of Flax fibres

	Diameter range in µm	Diameter in µm	Young modulus in MPa	Strain at failure in %	Tensile strength in MPa
Raw flax	20 – 22.5	21.57 (± 0.95)	64098 (± 13650)	2.93 (± 0.74)	1499 (± 346)
	22.5 - 25	23.86 (± 0.68)	51279 (± 12017)	3.34 (± 0.71)	1317 (± 529)
Dried flax	20 – 22.5	20.94 (± 0.76)	59240 (± 19363)	2.07 (± 0.30)	870 (± 266)
	22.5 - 25	23.77 (± 0.72)	58656 (± 15859)	1.74 (± 0.37)	711 (± 251)

Keeping in mind the standard deviation, results in table 1 highlight that drying cycle do not induce a significative evolution of Young's modulus. Indeed Young's modulus is a function of the volume

fraction of cellulose (reinforcement) while its degradation is triggered around 230°C [13].
Although Young's modulus is not influenced, mechanical behaviour is altered by drying process. In both cases, stiffness increases with strain which is explained by mesofibrills reorientation during tensile test. Several work such as those of Keckes et al [14] on wood and Baley et al [4] on flax fibre emphasize this fact by means of different experimental techniques such as synchrotron or cyclic loading. Reorientation during tensile loading could induce reduction of microfibrillar angle.
Astley and Donald [15] have shown by X-ray scattering that during tensile loading, strain induces cristallization of amorphous phase of meso-fibrills. According to Hearle [16] deformation mechanism during tensile loading follow a specific chronology :
First, length of non-cristalline part of mesofibrill increases. Then extension like spiral spring with flexural or twisting of meso-fibrills occurs in association with their volume reduction. Finally non crystalline area is sheared to follow the new fibrillar architecture. Shearing of the polysaccharide network (xyloglucans and galactans) beyond this shear strength induces its viscous flow due to hydrogen bond breakage. Load transfer is still possible between components thanks to stick-slip or velcro™ mechanism [17]. This bevahiour is, for flax fibres, due to xyloglucans and galactans ability to entangle and disentangle with pectin matrix. Finally cellulose fibrils will align themselves in the solicitation direction.
Figure 3 shows the evolution of Young's modulus as a function of the strain for raw and dried flax fibres.

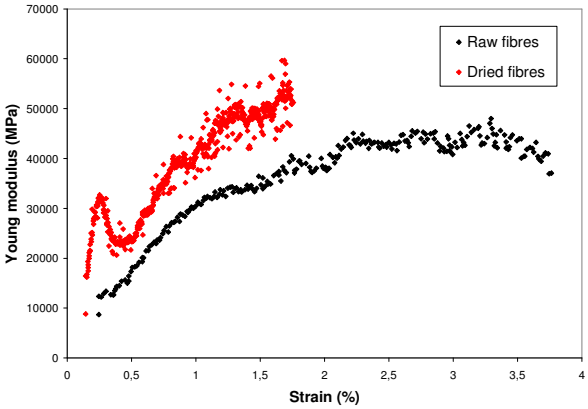

Fig 3. Typical evolution of Young's modulus as a function of strain. Raw fibre (black) and dried fibre (red)

For raw flax fibres, Young's modulus follows a two-part curve. Change of slope is considered as the beginning of irreversible damage. Dried flax fibres exhibit dramatic evolution of stiffness with an important yield observed for lower strain values. Again, this yield or threshold corresponds to the beginning of damage mechanism.
Figure 4 shows an example of damage undergone by flax fibres during tensile tests.

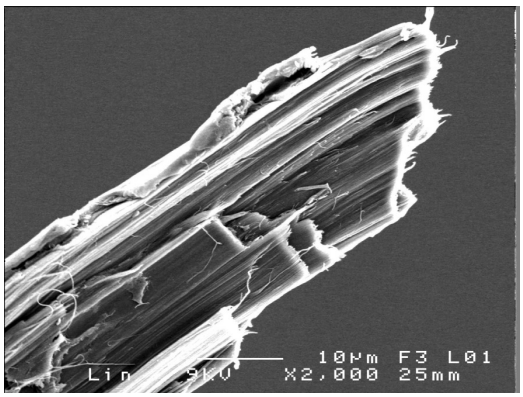

Fig. 4. *Break area of a flax fibre after a tensile test.*

The fracture surface of a flax fibre highlights the secondary cell wall with a structure of unidirectional composite, mesofibrils are aligned with the axis of the fibre .
To analyse the effect of drying, normal stress in the fibre and shear stress are calculated using equation (1).

$$\tau_{LT} = \frac{F\sin(2\theta)}{2S} \qquad (1)$$

With F the load in Newtons, θ the microfibrillar angle (θ = 10°) and S the cross section. Table 2 show the evolution of shearing stress at the change of slope

Table 2 Influence of drying on tensile and shear properties of S2 cell wall of flax fibres

Material	Diameter range in µm	Tensile strength in MPa	Normal stress at yield in MPa	Shear stress at yield in MPa
Raw flax	20 – 22.5	1499 (± 346)	292 (± 82)	50 (± 14)
	22.5 - 25	1317 (± 529)	225 (± 109)	39 (± 20)
Dried flax	20 – 22.5	870 (± 266)	61 (± 29)	10 (± 5)
	22.5 - 25	711 (± 251)	48 (± 27)	8 (± 4)

Results from table 2 show that normal stress at yield is around 20% of tensile strength for raw fibres while shearing strength is in the same range as those of common reinforced polymer such as glass polyester or glass/epoxy [18]. Drying induces a reduction in normal stress as well as shear stress (Table 2). Furthermore normal stress for dried flax fibres is around 6% of their tensile strength.

The hypothesis made here relies on the basis that the stress at the change of slope corresponds to the stress required to induce cellulose fibrils sliding. In wood system, stick slip mechanism is influenced by hemicelluloses attached to cellulose fibrils which form a hydrated gel network able to entangle and disentangle with the rest of the matrix [17]. Thus water evacuation by drying will influence the entanglement ability of hemicelluloses and thus load transfer between cellulose fibrils and polysaccharide matrix.

Drying can also induce physical and chemical change of components (cellulose, pectins, and hemicelluloses) [13] as well as thermal residual strain.

4. Conclusion

Growing interest is focused on natural fibres reinforced composites. Indeed flax fibres can reinforce polymer matrix, decrease environmental impacts and produce recyclable and compostable when associated with compostable polymers. However natural fibres contain certain amount of water which may be a problem for compounders. Indeed bad interfacial bonding and porosity are expected. Thus most of time natural fibres are dried before mixing with the polymer. Results of the present study have shown that drying during 14 h at 105°C involves loss of strength (- 44%) and strain (- 44%). Change of mechanical behaviour is also observed. Indeed hierarchical composite structure of natural fibres induces, when loaded in tensile mode, a reduction of microfibrillar angle and increase of stiffness. Analysis of stiffness/strain curves let appear a special behaviour with damage threshold corresponding to cellulose fibrils sliding due to shearing forces. Determination of this threshold make possible to estimate shear strength of S2 Cell wall (secondary cell wall). Drying has been proven to decrease normal stress and shear stress at yield.

Thus for optimal use of natural fibre as composite reinforcement, it is useful to check the thermal cycle to keep the whole mechanical potential of natural fibres.

This study has highlighted that loss of water alter mechanical properties of natural fibres. Now further work is needed to understand the effect of drying on their surface properties.

5. References

1 Wang HH, Drummont JG, Reath SM, Hunt K, and Watson PA, (2001), "An improved fibril angle measurement method for wood fibres";*Wood Science and Technology*, 34: p.493--503

2 Morvan C, Andème-Onzighi C, Girault R, Himmelsbach DS, Driouich A, and Akin DE, (2003), "Building flax fibres: more than one brick in the walls";*Plant Physiology and Biochemistry*, 41, 11-12: p.935-944

3 Gorshkova T, Wyatt S, Salnikov V, Gibeaut D, Ibragimov M, Lozovaya V, and Nicholas C, (1996), "Cell-Wall Polysaccharides of Developing Flax Plants";*Plant Physiology and Biochemistry*, 110: p.721-9

4 Baley C, (2002), "Analysis of the flax fibres tensile behaviour and analysis of the tensile stiffness increase";*Composite Part A: Applied Science and Manufacturing*, 33, 7: p.939-948

5 Charlet K, Baley C, Morvan C, Jernot JP, Gomina M, and Bréard J, (2007), "Characteristics of Hermès flax fibres as a function of their location in the stem and properties of the derived unidirectional composites";*Composite Part A: Applied Science Manufacturing*, 38, 8: p.1912-1921

6 Le Duigou A, Davies P, and Baley C, (2011), "Environmental impact analysis of the production of flax fibres to be used as composite material reinforcement";*Journal of biobased materials and bioenergy*, 5: p.1-13

7 Burgert I, (2006), "Exploring the micromechanical design of plant cell walls";*American Journal of Botany*, 93, 10: p.1391-1401
8 Fratzl P, Burgert I, and Gupta H, (2004), "On the role of interface polymers for the mechanics of natural polymeric composites";*Phys. Chem.Chem.Phys*, 6: p.5575-5579
9 Trouy-Triboulot M and Triboulot P, "Matériau bois- Structure et caractéristiques";*Techniques de l'ingénieur*, C 925: p.1-26
10 Baley C, Morvan C, and Grohens Y, in Polymer-Solvent complexes and intercalates V, Y.Grohens, Wiley-VCH: Lorient. 2004,
11 Le Chat C, Bunsell A, Davies P, and Piant A, (2006), "Mechanical behaviour of polyethylene terephthalate and polyethylene naphthalate under cyclic loading";*Journal of materials science*, 41, 6: p.1745-1756
12 Andersons J, Porike E, and Sparnins E, (2009), "The effect of mechanical defects on the strength distribution of elementary flax fibres";*Composites Science and Technology*, 69, 13: p.2152-2157
13 Van de Velde K and Baetens E, (2001), "Thermal and Mechanical Properties of Flax Fibres as Potential Composite Reinforcement";*Macromolecular Materials and Engineering*, 286, 6: p.342-349
14 Keckes J, Burgert I, Fruhmann K, Muller M, Kolln K, Hamilton M, Brughammer M, Roth S, Stanzl-Tschegg S, and Fratzl P, (2003), "Cell-wall recovery after irreversible deformation of wood";*Nature Materials*, 2: p.810-814
15 Astley A and Donald A, (2001), "A small angle scattering X-ray study of the effect of hydration on the microstructure of flax fibers";*Biomacromolecules*, 2: p.672-680
16 Hearle J, (1963), "The fine structure of fibers and crystalline polymers. III. Interpretation of the mechanical properties of fibers";*Journal of Applied Polymer Science*, 7: p.1207-23
17 Altaner CM and Jarvis MC, (2008), "Modelling polymer interactions of the molecular Velcro' type in wood under mechanical stress";*Journal of Theoretical Biology*, 253, 3: p.434-445
18 Pierron F and Vautrin A, (1996), "The 10° off-axis tensile test : A critical approach";*Composite Science and technology*, 56: p.483-488