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Analysis of flax fibres viscoelastic behaviour at micro and nano scales

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ABSTRACT

In glass or carbon fibres reinforced plastics, creep or stress relaxation, arise from the polymeric nature of the matrix. Plant fibres, used in bio-composites, are also polymers. Therefore, the issue of their service life requires studying the viscoelastic behaviour of both the matrix and the fibres. In this study, we investigate, at different length scales, the response of *elementary* flax fibres to tensile tests, as well as to nano-indentation tests on their secondary cell walls. The results of these experiments are then analysed via linear viscoelastic rheological models and identification procedures. The values of the identified parameters (relaxation time, viscosity and elastic stiffness) are discussed in relation to the microstructure of the flax fibre (cellulose microfibrils, hemicelluloses and pectins). The nano-indentation technique provides much more deterministic results than tension tests on an entire fibre. The scale of the secondary wall cell is then relevant to assess the viscoelastic behaviour of the fibres.

1. Introduction

In recent years, many research and industrial developments have been devoted to the integration of plant fibres as composite polymer reinforcement. In Western Europe, the most interesting ones are flax or hemp fibres due to their high-performance specific mechanical properties [1,2] as well as their environmental and ecological benefits [3]. The mechanical performances and behaviour of plant fibres are highly dependent on their microstructure and biochemical composition [5]. Flax fibres exhibit a complex, hierarchical and multi-component structure; they could be considered, themselves, as complex composite materials [6]. While the mechanical properties of these fibres, including elastic stiffness or strength, have been extensively investigated, their time-dependent behaviour has been hardly addressed. However, the susceptibility to time-dependent phenomena raises major and legitimate concerns associated with the use of these materials in service as reinforcements of polymer matrices. The polymeric nature of the matrix in usual glass or carbon fibre reinforced plastics is responsible for their susceptibility to creep, not the ceramic nature of the fibres (see e.g. [7]). Yet, for composites for which the reinforcement is also of polymeric nature, the viscoelastic contribution of these natural fibres to the overall creep, relaxation or rate-dependent behaviours may also be of importance. An old example of a study of the time-dependent mechanical behaviour in plant fibres is given in [8]. Since then, little attention has been paid to the viscoelastic behaviour of *elementary* plant fibres even if very recent studies on fibre bundles exist [9,10].

Fig. 1 presents the general structure of a flax fibre. Fibres commonly have a polygonal section, and are arranged into concentric cell-wall layers with a small channel in the middle, called the lumen. The outer cell wall is called the primary cell wall and is ~200 nm thick. This wall has a structural role by ensuring the fibre length continuity and is made of pectins, poorly crystallized cellulose, and xyloglucans as the main hemicelluloses [11]. The bulk of the fibre cell walls is made by the secondary wall, and is divided into three different layers – S1 (0.5–2 μm thick), S2 (5–10 μm) and S3 (0.5–1 μm) – and provides the reinforcement of the plant structure. The main layer, S2, representing around 80% of the total section, is made of highly crystalline cellulose fibrils spirally wound in a matrix of amorphous hemicelluloses and pectins [12]. The cellulose fibrils make a ~9° angle with the axis of the fibre [5] – which is called micro-fibrillar angle (MFA) – and their crystallisation content is ~65% for the secondary cell wall fibrils [13].

The objective of this paper is therefore to study the viscoelastic behaviour of such flax fibres at different length scales. The mechanisms at stake are the instantaneous elasticity, the delayed one and creep. The inherent complexity of their microstructure will make us investigate creep, relaxation, recovery and strain-rate

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sensitivity, using different loading conditions and tested volumes, namely tension for the fibres and nano-indentation for the secondary cell wall. Nano-indentation studies have recently been used to study the viscoelastic behaviour of different kinds of materials including polymers [14–16], silicate glasses [17], amorphous alloys [18,19] or wood fibres [20,21]...but never, to our knowledge, on flax fibres. This work is therefore a first attempt of doing so, including a mechanical analysis. The results will be discussed at the light of existing knowledge on the microstructure of flax fibres and their deformation mechanisms.

2. Materials and methods

2.1. Materials and samples

Linum usitatissimum (flax) fibres of Hermes variety were harvested in Normandy (North-West of France) at the end of August 2003. They were sowed at the beginning of April and pulled in July. After pulling, plants were laid over the field for drying during four weeks to allow dew retting, that is the development of fungi within the stem, which degrades their cortical tissues and further facilitates the mechanical extraction of the fibres. Then, the fibres were scutched and carded. Samples for the tension tests were isolated from the bundle by hand. Due to their short length (about 30–40 mm), a gauge length of 10 mm was chosen. They have a diameter of 10–20 μm. Three measurements obtained by optical microscopy were carried out along each fibre length to determine the mean diameter. The initial cross-section area, S_0, was calculated by considering the fibre as axisymmetric, via this diameter. As for the samples for the nano-indentation tests, a complete stem without any fibre extraction was embedded in epoxy resin. Using an ultramicrotomic apparatus minimised the stem surface roughness, which was found to be 3–5 nm, measured by using Atomic Force Microscopy.

2.2. Mechanical experiments

Tensile tests on single fibres were carried out at controlled temperature (23 °C) and relative humidity (48%). Before the test, the fibre is glued on a paper frame with vinyl paper glue. The latter is chosen not to affect the mechanical response of the fibre in tension. The paper frame is then clamped on a universal MTS type tensile testing machine equipped with a 2 N capacity load cell, with an accuracy of 0.01%. After the edges of the frame are cut, the tests were performed. The mechanical analysis of tension is made using the engineering strain and the engineering stress, since small strains will be developed. The strain is $\varepsilon = (l - l_0)/l_0$, where l_0 is the initial length and l the current length, adjusted to take into account the compliance of the traction device (0.1246 mm/N). The stress is calculated from $\sigma = F/S_0$, where F is the measured force. The accuracy of the displacement sensor is 1 μm.

Due to the nature of the fibres, it is necessary to carry out an adequate number of experiments to obtain meaningful statistics of the mechanical behaviour. We therefore made ~100 monotonous tensile tests at a constant displacement rate of 1 mm/min (strain rate of $1.67 \times 10^{-3}\ s^{-1}$) to extract the usual mechanical properties (tensile elastic modulus, fracture strength and fracture strain). The viscoelastic behaviour was also studied by performing a non-monotonous loading on seventeen different fibres. This loading type consists into six steps: a first stage with a monotonous loading at a strain rate of $10^{-3}\ s^{-1}$ up to a strain of 0.4%, followed by a second step during which this latter strain value is held constant (relaxation step) for 50 s. The third and fourth steps are the same as the first and second ones for a strain rate of $10^{-4}\ s^{-1}$, a strain value of 0.8% and a holding time of 500 s, respectively. Again for the fifth and sixth steps with a strain rate of $10^{-5}\ s^{-1}$, a strain value of 1.4% and a holding time of 1000 s, respectively. This loading type allows for characterising the two main features of viscoelasticity: the strain-rate dependence (even steps) and the time-dependence (odd steps, further referred to as A, B and C).

As for the nano-indentation tests, samples were positioned into the chamber of a nano-mechanical testing device (Hysitron TI 950) during 12 h to ensure steady thermal and moisture conditions. A three-side pyramid (modified Berkovich) diamond indenter was used with the Standard head. The area function for the tip was calibrated by using a standard sample (fused quartz). The load on the sample (P) and the penetration depth (h) are monitored throughout the test. The indentation direction is perpendicular to the cross section. Before each indentation test, a particular cell is targeted by optical microscopy. Then specific locations are selected in the secondary layer (S2) of the secondary cell wall, far enough from both the cell boundaries and the lumen. The viscoelastic behaviour of the secondary wall was investigated by using two different methods. The first one uses the tip to monitor the creep and relaxation stages. It is carried out using the following sequence:

1. Thermal drift is measured during 60 s. It is typically below 0.05 nm/s.
2. A maximum load of 600 μN is applied in 10 s.
3. This load is held constant during 60 s (creep or holding stage).
4. The load is removed in 10 s, leaving a residual depth, h_f, of ~170 nm.
5. A very low load (2 μN) is imposed to the surface to monitor the recovery stage.

During the creep stage (step 3), the changes in depth with time, corrected by the thermal drift (step 1) are monitored. During the

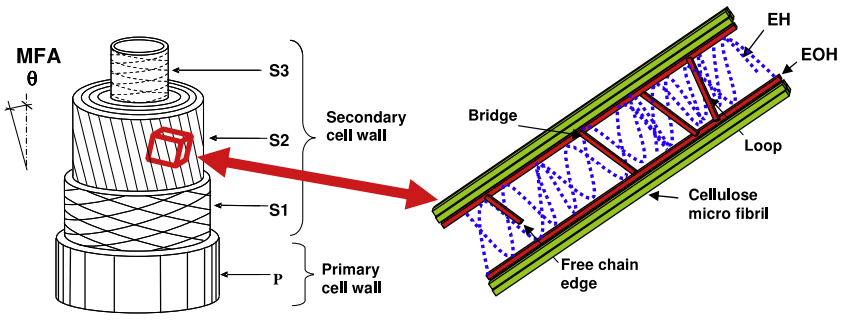

Fig. 1. Schematic representation of a flax fibre showing the helix arrangement of cellulose fibrils and S2 layer structure (adapted from [5]). MFA is the microfibrillar angle, while EH and EOH denote respectively the structural and non structural hemicelluloses and pectins. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)