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Plant cell walls to reinforce composite materials: Relationship between nanoindentation and tensile modulus

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ABSTRACT

Throughout this study, different plant fibres, used as polymer reinforcement, were tested by quasi-static tensile and nanoindentation tests to obtain their modulus using these two methods. Major differences of stiffness were found due to their different structures and morphologies. As example, tensile and nanoindentation moduli for sisal fibres were and 25.0 ± 12.9 GPa and 10.2 ± 1.7 GPa, respectively, whereas they were 52.4 ± 13.2 GPa and 18.9 ± 1.8 GPa for Eden flax fibres. A correlation between these two moduli was established; thus by an inverse method, we estimated the longitudinal stiffness of softwood fibre, for which the tensile test is delicate, mainly due to the short length of the fibre.

1. Introduction

In injection moulding, thermoplastics can be reinforced with short plant fibres due to their good specific mechanical properties [1]. These plant fibres mainly come from leaves (sisal), mesocarp (coir) or stems (flax, hemp or jute) and are essentially composed of the S2 layer of the secondary wall [2] with a central cavity called a lumen. The cell walls are generally composed of cellulose fibrils, spirally arranged in a matrix of hemicelluloses, pectins and lignin. The cellulose fibrils orientation is defined by their micro fibrillar angle (MFA). According to the species and varieties of plants, the fibre structure and composition change and these intrinsic differences influence their mechanical properties [3]. These differences are strongly related to the fibre function in the plant. Thus, fibres from stems such as flax or hemp are loaded by the plants movements and play role of supporting tissue [4], exhibiting better mechanical performances.

Elementary flax fibre and bundles can be tensile characterized according to NF T25-501-2 and NF T25-501-3 standards, respectively. For an elementary fibre the free length is 10 mm. This is the limit for very short single fibres such as wood (softwood Lf~3.3 mm [5]), which requires specific experimental systems [6].

It is also possible to estimate the cell walls stiffness by nanoindentation. Due to the inclination of the flanks of the indenter, the measured stiffness takes into account longitudinal and transversal moduli, giving an underestimated modulus value compared to the tensile test, especially for anisotropic materials [7] such as the plant cell walls.

In this study many plant fibres of different species were characterized by a tensile test. Then, the nanoindentation moduli were determined on the same plant cell walls. The correlation between these two moduli was established to estimate, by reverse method, the tensile modulus of wood fibres.

2. Materials and methods

The plant fibres used in this study are textile flax (Hermes, Eden and Alize), oleaginous flax (Oliver) and Hemp (Fedora 17) cultivated in France. Sisal fibres come from Tanzania, bamboo from Thailand, Coir from Indonesia. The varieties of jute fibre are Tossa from the Jamalpur and Faridpur districts in Bengal. Softwood fibres were extracted from Woodforce® pellets.

The determination of the tensile properties was made in accordance with the NF T 25-501-2 (elementary flax fibre) and NT T25-503-3 (bundle flax fibres) standards, taking into account the loading frame compliance. For all plant fibres a 10 mm free length was chosen to allow suitable comparisons. Elementary flax and hemp fibre lengths are above this value unlike the other fibres selected [5] which are in the form of bundles. The average apparent diameter (from 3 measurements) was determined under a microscope. The frame was clamped on a universal MTS-type tensile-testing machine equipped with a 2 N capacity load cell, and

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loaded at a constant crosshead-displacement rate of 1 mm/min up to rupture in a laboratory with a controlled temperature (23 °C) and relative humidity (48%).

Nanoindentation measurements were made on the fibre sections after inclusion in an epoxy resin and polishing to 1-µm. We used a commercial nanoindentation system (Nanoindenter XP, MTS Nano Instruments) at room temperature (23 ± 1 °C) with a continuous stiffness measurement (CSM) technique, equipped with a three-side pyramid (Berkovich) indenter. We worked with 3-nm amplitude, 45 Hz oscillations using a 0.05 s-1 loading rate. Measurements were taken at depths to 120 nm. For each sample, around 50 indents were performed in 8–10 distinct fibres. Indent positions were checked by AFM imaging using an *in-situ* DME (Hannover, Germany) Dualscope 95–200 AFM equipment.

3. Results and discussion

3.1. Tensile properties of plant fibres

Table 1 shows the tensile and nanoindentation properties of the various plant fibres. Measured diameter values are consistent with literature as well as the Young modulus obtained by the tensile test [5]. The property difference between the fibre varieties are explained by their MFA but also by the biochemical structure of the cell walls. Fibres having good mechanical properties (flax, jute, hemp) have a MFA between 8° and 11°. Conversely coir fibres have a high MFA (39–40° [8]). Additionally, flax fibres have an average cellulose rate of 68% [5] against 32% [5] for coir. Furthermore, the nature of S2 incrusting polysaccharides varies considerably depending on the fibre variety. Thus, for the normal wood, coir or jute, the main constituents are lignin and xylan [3] while for flax, hemp, or even tension wood or bamboo, the walls are gelatinous types and contain a high proportion of galactan whose major role in flax fibre stiffness was demonstrated by Gorshkova and Morvan [9].

3.2. Nanoindentation experiments on the plant cell wall

The indentation moduli (IM) are shown in Table 1. To illustrate, Fig. 1 shows AFM images taken after indentation in the S2 layer of flax and wood. Both a large diameter and lumen can be observed for wood, compared to flax. Wood fibre appears lightly crushed, which is due to the manufacturing processes of Woodforce® pellets.

As explained in the introduction, the indentation modulus is logically lower than that obtained by traction on elementary fibres [7]. We can also assume that when pushing the indenter into the cell wall, there is a local separation of microfibrils, this cleavage phenomenon can amplify this underestimation. Significant variations could be observed between fibre species and even for a same plant (flax for example), underlining the cell walls structural and biochemical variations. According to Eder et al. [10], IM is predominantly governed by the cellulose content and by their MFA. The lower the MFA the more the fibrils will be loaded during the test, obtaining a higher IM.

Nevertheless the measurements were performed under the same conditions for all fibres, allowing a relevant stiffness comparison. We can note that for softwood, a nanoindentation modulus of 15.1 ± 2.6 GPa was found, which correlated well with the results of Gindl et al. [11] (15.34 GPa on spruce fibres).

3.3. Relationship between nanoindentation and tensile modulus

Fig. 2 compares the tensile and nanoindentation modulus of plant fibres. Gindl also established this correlation for regenerated cellulose fibres [7]. Our plant fibres exhibit various wall structures, explaining both the non-linearity and dispersion. Indeed, fibres having the greatest stiffness are also the most anisotropic, which generates a significant gap between the tensile and nanoindentation modulus.

The structural difference can be underlined by the recovery measurement of indents; Fig. 3 shows indent profiles performed on flax and wood by AFM imaging, one hour after indentation. The average depths of indents on flax and wood are 48.2 ± 2.3 and 67.6 ± 3.6 nm (average of 5 indents), respectively, showing a higher recovery level for the wood than for flax cell walls. This can also be observed on the size of the indent (Fig. 2).

Unlike flax, wood cell walls contain a higher amount of non-cellulosic polymers (hemi-cellulose, lignin) than crystalline cellulose, giving a more pronounced elastic behaviour and better recovery for flax. Additionally the lower MFA of the flax enhances the elastic return of the wall [12].

The correlation curve equation (Fig. 2) was used to estimate a tensile modulus value of the wood fibres; we obtained 34 GPa which is above the literature values. Thus, Kretschann et al. [14] measured a modulus between 11.9 and 25.4 GPa and Burgert et al. [6] 22.6 GPa. This overestimation may be caused by the fact that the correlation curve was performed with cell walls, which do not have the same mechanical anisotropy, inducing variations of the

Table 1
Tensile and nanoindentation properties of plant fibres.

	Tensile test					Nanoindentation	
	Fibers number	Diameter (µm)	Efl (GPA)	σr (MPa)	εr (%)	Indents number	Indentation modulus (GPa)
Hermes (b)	31	20.1 (± 4.1)	46.9 (± 15.9)	755 (± 364)	1.6 (± 0.5)	59	16.9 (± 1.74)
Hermes (m)	37	19.6 (± 6.7)	63 (± 35.8)	1454 (± 835)	2.3 (± 0.6)	69	19.8 (± 2.6)
Hermes (h)	36	19 (± 3.5)	59.1 (± 17.5)	1129 (± 390)	1.9 (± 0.4)	51	18.5 (± 2.5)
Oliver (b)	83	18.3 (± 5)	47.2 (± 21.3)	751 (± 413)	1.67 (± 0.6)	67	19.1 (± 4.2)
Oliver (m)	76	17.5 (± 3.6)	50.0 (± 27.2)	802 (± 381)	1.75 (± 0.78)	61	15.7 (± 2.8)
Oliver (h)	61	20.7 (± 3.7)	54.5 (± 32.5)	960 (± 692)	2.0 (± 1.2)	65	16.1 (± 1.6)
Eden Flax (m)	58	15.2 (± 2.6)	52.4 (± 13.2)	912 (± 339)	2.3 (± 0.9)	60	18.9 (± 1.8)
Alize Flax (m)	65	16.3 (± 4.8)	49.5 (± 20)	803 (± 342)	2.3 (± 1.7)	58	19.7 (± 2.6)
Hemp (m)	43	16.1 (± 4)	33.8 (± 12.2)	489 (± 233)	2.5 (± 1.3)	48	13.4 (± 2.3)
Jute Faridpur	81	45.1 (± 12.7)	21.3 (± 12.2)	277 (± 154)	1.79 (± 0.6)	68	14.5 (± 2.5)
Jute Jamalpur	52	45.4 (± 12.9)	24.4 (± 12.0)	280 (± 178)	1.74 (± 0.6)	63	13.1 (± 1.6)
Sisal	32	25.4 (± 11.17)	25.0 (± 12.9)	526 (± 290)	2.3 (± 0.3)	51	10.2 (± 1.7)
Bamboo	35	289 (± 88)	21.2 (± 11.5)	479 (± 206)	2.9 (± 0.5)	57	14.9 (± 2.1)
Coir	54	219 (± 83)	17.3 (± 4.2)	110 (± 17)	3.7 (± 0.8)	45	6.0 (± 1.6)
Wood	–	–	–	–	–	67	15.1 (± 2.6)

Hermes and Oliver fibers were collected from the bottom (b), middle (m) and height (h) part of scutched.