MECHANICAL BEHAVIOUR OF HEMP FIBRE COMPOSITES IN RELATION TO THEIR MICROSTRUCTURE BY MICRO STRAIN MAPPING, COMPUTED TOMOGRAPHY, AND BIOCHEMICAL ANALYSIS

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Abstract
This manuscript describes the effects of alterations in biochemical composition on structural morphology and the mechanical behaviour of elementary and technical fibres of hemp used for composite applications. First, the strength and apparent Young's modulus distribution of technical fibres of hemp of 96 hemp samples, corresponding to 32 different hemp accessions cultivated in 3 locations, were analysed using Weibull distribution. From these, 2 samples (one with high and one with low fibre strength) were selected for further analysis. Next, full-field strain measurement at the micro-scale during tensile loading was used for evaluating both, the stress-strain behaviour at a global scale and the local mechanical behaviour heterogeneity at a micro-scale, along elementary and technical fibres of hemp. At the composite level, the local behaviour of each phase of the composite (fibre and matrix) and of the fibre/matrix interphase during a transversal 3 point bending test were characterized.

Results show that the strength of technical fibres of hemp is highly dependent on the shear strength between elementary fibres, which itself is related to the biochemical composition of the middle lamellae. A correlation between the strength of a technical fibre and their elementary fibres was also observed. At the composite level, the relation of the composite mechanical behaviour (Young's modulus and strength) with the technical or elementary fibre mechanical behaviour is complex and might depend on the combination of multiple factors such as the matrix (thermoset or thermoplastic), or the technical fibre sample employed (weak or strong) and the level of fibre-matrix wetting (impregnation) and adhesion.

1. Introduction

Technical natural fibres are being increasingly used as the reinforcing phase in long fibre reinforced composites. However, it is not clear whether the tensile behaviour of the technical fibre or the elementary fibre (or a combination of both) is predominant in order to predict the composite behaviour [1].

The hierarchical organization of hemp fibre composites can be characterized at 3 different levels: composite, technical fibre, and elementary fibre (Fig. 1). At the composite level, the mechanical behaviour depends on the properties of the reinforcing fibre, the matrix and the fibre-matrix interface [2]. However, natural fibres, such as hemp, are composite materials themselves showing at least two different levels of hierarchy.

The structure of a technical hemp fibre consists of elementary fibres with thick cell walls, which are surrounded by a soft amorphous lignin or pectin rich layer (middle lamella), and the cell wall is, in turn, composed of several layers of rigid cellulose microfibrils oriented at different angles, and joined by hemicelluloses and lignin as matrix material [3, 4].

Mechanical properties such as stress-strain behaviour or the elastic modulus differ greatly at different hierarchical levels. Even though natural fibres and their composites exhibit a multi-level microstructure, standard macroscale methods for measuring their tensile properties give global strain only. This research presents a novel experimental approach to characterize the non-linear behaviour of different technical and elementary hemp fibre samples, and their composites, by combining standard tensile tests with a detailed full-field strain map at the micro-scale during tensile loading. At the composite level, the local behaviour of each phase of the composite (fibre and matrix) and of the fibre/matrix interphase during a transversal 3 point bending test (Fig. 1c) are characterized.

The objective of this research is to study the non-linear tensile behaviour of elementary and technical fibres of 2 hemp samples selected from a collection of 96 samples (resulting from 32 accessions cultivated in 3 different locations), as well as their composites, in order to explain the responsible mechanisms for their performance. The selected samples revealed the lowest and highest strength from the strength distribution of technical fibres of hemp of the 96 different samples, which were analysed using the Weibull distribution and one-way ANOVA statistical analysis. Longitudinal strength and transverse strength of thermoset (Epoxy) and thermoplastic (Polyvinylidene fluoride, PVDF) composites of both hemp samples were also measured by three point bending test.

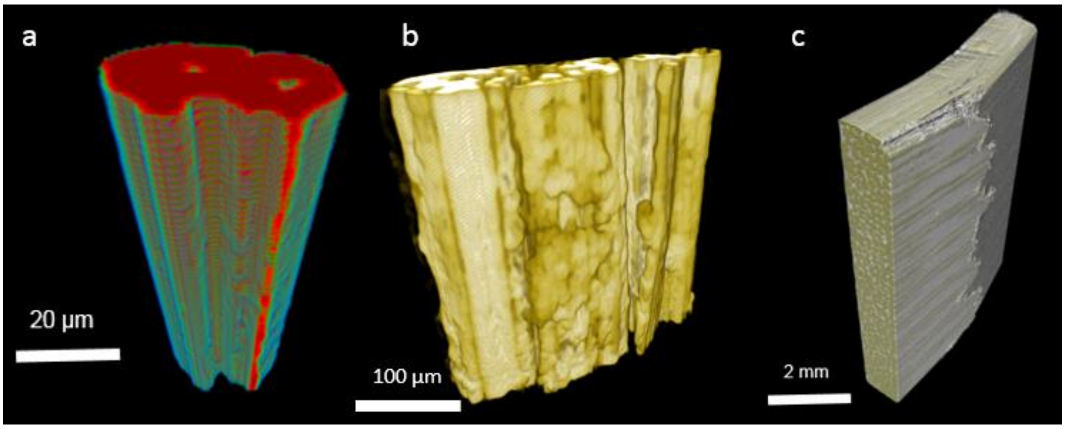

Figure 1. Three-dimensional reconstructions of an elementary fibre (a) and a technical fibre (b) of hemp. A typical hemp fibre reinforced composite sample undergoing deformation (3 point bending test) (c).

2. Materials and Methods

2.1. Materials

In the framework of the FP7 - MultiHemp project (Multipurpose hemp for industrial bioproducts and biomass), 32 hemp fibre accessions[1] were provided by partners of the consortium. Each accession was cultivated at three different geographical locations (The Netherlands, Italy, and France), making a total of 96 samples. Then, a sample is a particular accession linked to a specific location of growth, and the elements of the samples are individual technical fibres. More information about the MultiHemp project and the genome-wide association mapping trial of the 96 accessions can be found in [5].

2.2. Tensile Testing and 3-point bending test

Twenty randomly selected technical fibres for each sample were visually inspected to verify the absence of major damage, and then conditioned at 20° C and 50% RH for more than 3 days. The technical fibres were then weighed and the cross-sectional area of each individual technical fibre was calculated using its density, mass and length, assuming that the technical fibres have a constant cross-section. Only fibres with cross–sectional areas within 0.005 and 0.025 mm² were used. A gauge length of 20 mm was used for all the tests and the crosshead speed was 0.5 mm/min.

Unidirectional composites were prepared by compression moulding of stacks of prepregs consisting of technical fibres, sandwiched between thermoplastic films. The applied pressure was 10 bar and temperatures between 175◦C and 200◦C were used. Epoxy composites were prepared by vacuum infusion process. Flexural three point bending tests in transverse direction were performed on a universal testing machine (Instron 4426) based on ASTM D790, to obtain an estimation of the bond strength in tensile mode.

2.3 Strain Mapping

Two contrasting hemp samples, one with low and one with high technical fibre strength, were selected for DIC analysis: VDS-FNPC-243 and VDS-CRA-410 where VDS stands for the place of cultivation (VANDIJKE SEMO B.V., Scheemda) in the Netherlands, and FNPC-243 and CRA-410 for the owner (FNPC for Fédération Nationale des Producteurs de Chanvre, Le Mans, France, and CRA for Consiglio per la Ricerca in Agricoltura, Rovigo, Italy) and code of the accession respectively. Elementary fibres were also extracted from these samples for analysis.

A random speckle pattern is created on fibres by using an Airbrush with a spray nozzle of 0.15mm.

The main parameters for a suitable speckle pattern for digital image correlation (DIC) analysis consist of speckle size, randomness and distribution. A good pattern, as illustrated in Fig. 2, consists of evenly distributed and uniform speckles on the whole area to be analysed.

In order to evaluate if the speckle patterns were good enough for DIC analysis, two methods were implemented: pixel intensity histogram and strain deviation analysis [6, 7].

An acceptable speckle pattern will produce a Gaussian distribution when it is subjected to a pixel intensity histogram analysis (see Fig. 3 - Left).

[1] Accession: A distinct, uniquely identifiable sample of seeds representing a cultivar, breeding line or a population, which is maintained in storage for conservation and use.

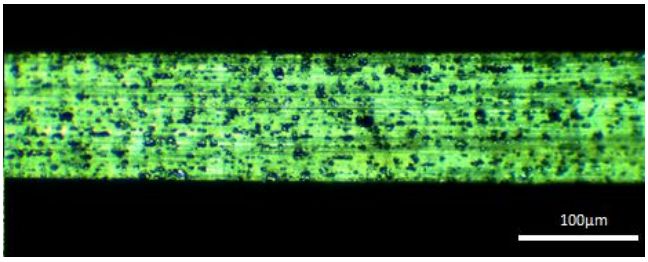

Figure 2. Example of a good speckle pattern on a hemp fibre.

Regarding the strain deviation analysis, a virtual and uniform deformation is applied on the image of the speckle pattern. Since the magnitude of the deformation is controlled and uniform, a homogeneous strain mapping over the entire image is expected. However, in reality digital resizing is not totally uniform, and local variations could be created depending on the method used for interpolation. Then, the quality of a speckle pattern could be evaluated by comparing strain deviations along a horizontal arbitrary chosen straight line on image length. A strain deviation analysis of a relatively good and relatively bad speckle pattern can be seen in Fig. 3 – Right.

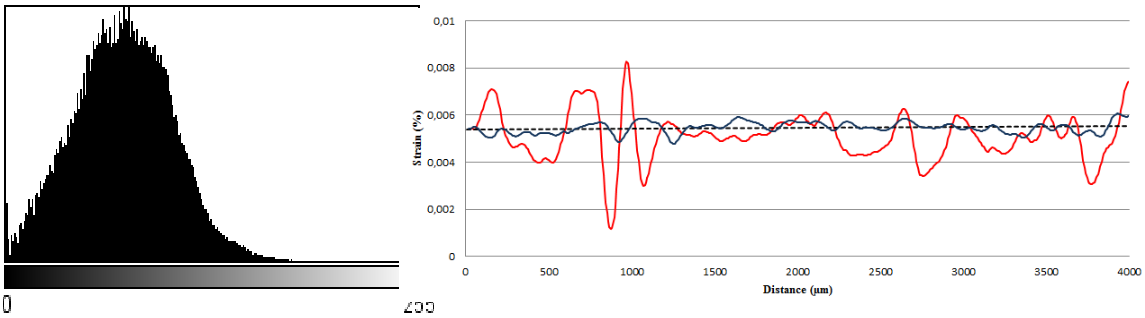

Figure 3. Pixel intensity histogram for the speckle pattern presented in Figure 1 (Left), and comparison of the strain deviation of a good (blue) and poor (red) pattern along the sample length (right).

A Motic microscope SMZ-171-TH with a Moticam camera of 10 MP of resolution were used to acquire the images. Ncorr software was used for DIC analysis.

2.4 Tomography

In order to evaluate the internal structure of the technical fibre, a SkyScan micro computed tomography (microCT) device (Bruker microCT, Kontich, BE) for scanning electron microscope (SEM) was used for obtaining 3D images of elementary and technical fibres of hemp, and a Phoenix NanoTom X-ray computed tomography equipment (General Electric Company, Fairfield, USA) was used for the composites.

For the SkyScan SEM microCT, a source voltage of 30kV, a source current of 90 µA and an exposure time of 4000 ms were used for scanning the technical fibres. The obtained voxel size was 700 nm.
For the Phoenix NanoTom, the applied voltage and current were 45 kV and 320 µA respectively. The exposure time was 700 ms and a frame averaging of 3 and image skip of 1 was applied. The obtained voxel size was 2.2 µm.

2.5 Biochemical Analysis

The cell wall extraction was performed using an alcohol-insoluble residue method (AIR) according to Pettolino et al. [8]. Two-step sulphuric acid hydrolysis at 72% and 4% (w/w) was performed to analyse the monosaccharide composition and lignin content of AIR, according to the US National Renewable Energy Laboratory [9]. More information regarding the complete procedure can be consulted in [10].

2.6 Statistics

A normality analysis was performed on tensile test data with a confidence interval of 95%. All results outside of this range were excluded, guaranteeing that no less than 16 technical fibres are finally used for Weibull analysis. Finally, a single factor analysis of variance (ANOVA) was used for verifying the statistical significant difference in the mean strength between different samples. Significance was set at $p < 0.05$ and error is reported as standard error of the mean value. The Tukey HSD (honestly significance difference) test was used to determine which specific groups differed from each other once a statistically significant difference was found by the one-way ANOVA test.

3. Results and Discussion

3.1 Technical Fibre Level

After Weibull analysis, the technical fibre tensile strength of the 96 samples were ranged between 400 MPa and 1011 MPa and the apparent Young's modulus (E) from 20 GPa to 40 GPa. The comparison carried out by one-way ANOVA statistical analysis showed that among the different tested hemp samples there is a significant difference in tensile strength between the 5 samples with the lowest and the 5 with the highest mechanical properties, at 95% confidence level. For the present study, the objective was to select one weak and one strong hemp fibre sample in order to assess differences in mechanical behaviour.

Two samples representing the 5 % extreme values of the strength distribution were selected. The sample VDS-FNPC-243 showed a Weibull strength value of 400.3 ± 127.2 MPa, while the sample VDS-CRA-410 showed a Weibull strength value of 838.5 ± 216.1 MPa. These two samples will be further referred to as the weak and strong samples, and their elements as the weak and strong technical fibres, respectively.

The stress-strain tensile behaviour at a global scale (Fig. 4) and the local mechanical behaviour heterogeneity at the micro scale (Fig. 5) for both the weak and strong technical fibres were examined. DIC analysis revealed two different mechanisms of failure. In the case of the weak sample (Fig. 5), technical fibre failure takes place at the interphase that bonds elementary fibres together, producing a fracture relatively parallel to the tensile direction. The non-linear behaviour of the stress-strain curve is explained by the development of shear strain at the elementary fibre interphases from very low levels of global strain on, until fibre breakage occurs.

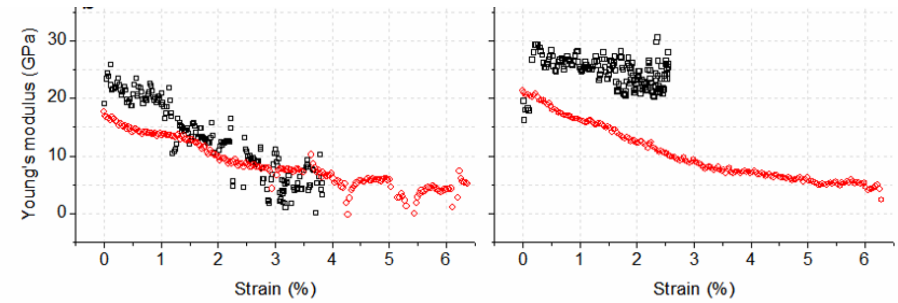

Figure 4. Typical global Young's modulus-strain curves for a weak (left) and a strong (right) technical fibre. Red circles stand for strain obtained by the displacement of the tensile machine crosshead, and black squares for strain obtained by DIC analysis.

On the other hand, strong technical fibres typically fail through elementary fibre breakage, producing a fracture perpendicular to the tensile direction. Shear strain only develops at a late stage of global strain, and produces the switch from quasi-linear to non-linear behaviour of the stress strain curve.

In general, strong technical fibres showed a more rigid behaviour during tensile tests (2.1 % strain to failure compared to 3.6 % for weak variant samples) due to a more compact micro structure, as revealed by tomography analysis, and a stronger interphase between the elementary fibres which is able to transfer the load to other elementary fibres. The composition analysis suggests that highly substituted polysaccharides content might have a positive effect on technical fibre strength, increasing the degree of ramification of RGI and as a consequence the amount of crosslinks in the pectic network of the middle lamella and of the primary cell wall.

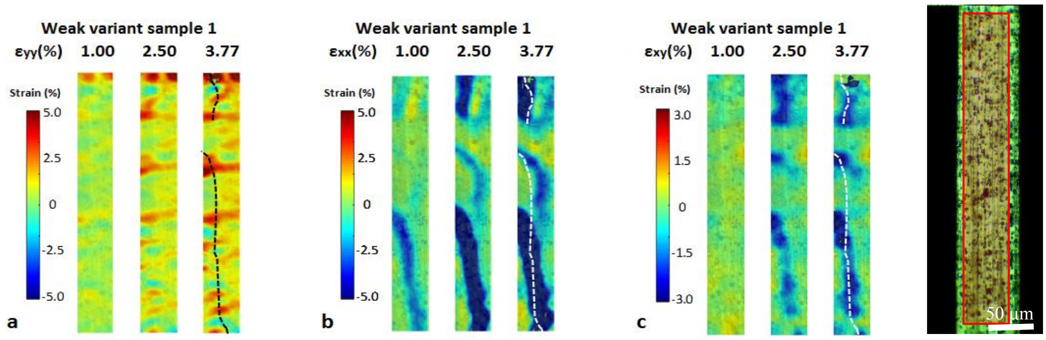

Figure 5. Full-field longitudinal, transversal, and shear strain analysis of a typical weak variant sample 1 (a, b, and c respectively).Strain maps represent the gradual evolution of local strain at 2 levels of global strain and the local strain distribution an instant before failure. The black and white dashed lines indicate the fracture lines visible after breakage of the technical fibre. Right image indicates the analysis area.

3.2 Elementary Fibre Level

The results showed that elementary fibres (see Fig. 6) generally exhibit slightly higher strength values (~824 MPa and ~664 MPa, for the elementary fibres extracted from strong and weak samples respectively) but higher apparent Young's modulus values measured by DIC analysis (~85 GPa and ~60 GPa for the elementary fibres extracted from strong and weak samples respectively) as their corresponding technical fibres (see previous section for strength and modulus values at the technical fibre level). A correlation between the strength of a technical fibre and their elementary fibres was also observed. A clear difference in strength was observed for the strong and weak elementary fibres. Previous studies have primarily attributed the difference between strong and weak technical fibres to the role of the interphase between the elementary fibres [10]. This study evinces that an elementary fibre extracted from a hemp accession with high strength also shows higher mechanical properties than an elementary fibre extracted from a technical fibre with lower strength.

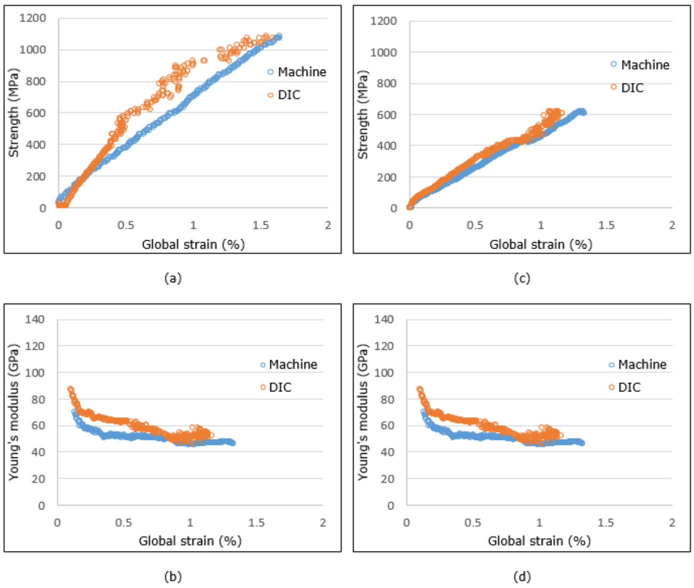

Figure 6. Typical stress-strain and tangent Young's modulus-strain curves for a strong (a and b respectively) and a weak (c and d respectively) elementary fibre. Blue dots stand for strain obtained by the displacement of the tensile machine crosshead, orange dots indicate strain obtained by DIC analysis.

3.3 Composite Level

At the composite level, the relation of the composite mechanical behaviour (Young's modulus and strength) with the technical or elementary fibre mechanical behaviour is complex and depends on the combination of multiple factors such as the matrix (thermoset or thermoplastic), or the technical fibre sample employed (weak or strong) and the level of fibre-matrix wetting (impregnation) and adhesion. Then it is not always the case that a weaker technical fibre reinforcing a composite will produce a weaker composite if compared with a composite reinforced with a technical fibre with higher mechanical properties. In the case of thermosets, the resin is able to penetrate the inter-fibre voids and good mechanical properties were obtained also for weak fibres, due to the fact that the elementary fibres are the ones that are being loaded. However, the mechanism is different for a thermoplastic, since very viscous matrices are not able to penetrate the inter-fibre voids, and then only the technical fibre are being loaded.

3. Conclusions

The analysis reveals 2 typical types of tensile stress-strain curves, and a complex and very irregular pattern of strain concentrations, which are associated to the elementary and technical fibre strength. The non-linear behaviour of the stress-strain curve is explained by the development of shear strain at the elementary fibre interphases. Micro tomography and biochemical analysis of the technical fibre microstructure showed that alterations in cell wall composition, in particular substitution of pectin, might lead to changes in the non-linear behaviour of technical fibres of hemp under tensile loading.

This study also reveals that an elementary fibre extracted from a hemp accession with high strength also shows higher mechanical properties than an elementary fibre extracted from a technical fibre with lower strength.

There is no correlation between the mechanical properties of strong and weak fibres with their composite mechanical behaviour, depending on the combination of multiple factors such as the matrix (thermoset or thermoplastic), and the level of fibre-matrix wetting (impregnation) and adhesion. If the matrix is able to reach and impregnate elementary fibres, then the composite mechanical properties are dominated by those of the elementary fibre.

Acknowledgments

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References

[1] Fuentes CA, Willekens P, Petit J, Thouminot C, Müssig J, Trindade L, et al. Effect of the middle lamella biochemical composition on the non-linear behaviour of technical fibres of hemp under tensile loading using strain mapping. Composites Part A: Applied Science and Manufacturing. 2017.
[2] Fuentes CA, Brughmans G, Tran L, Dupont-Gillain C, Verpoest I, Van Vuure A. Mechanical behaviour and practical adhesion at a bamboo composite interface: Physical adhesion and mechanical interlocking. Composites Science and Technology. 2015;109:40-7.
[3] Placet V, Cissé O, Boubakar ML. Nonlinear tensile behaviour of elementary hemp fibres. Part I: Investigation of the possible origins using repeated progressive loading with in situ microscopic observations. Composites Part A: Applied Science and Manufacturing. 2014;56:319-27.
[4] Fuentes CA, Tran LQN, Dupont-Gillain C, Vanderlinden W, De Feyter S, Van Vuure AW, et al. Wetting behaviour and surface properties of technical bamboo fibres. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2011;380(1-3):89-99.
[5] MULTIHEMP. Multipurpose hemp for industrial bioproducts and biomass (Report). Community Research and Development Information Service - European Comission. 2017;http://cordis.europa.eu/project/rcn/104295_en.html.
[6] Berfield T, Patel J, Shimmin R, Braun P, Lambros J, Sottos N. Micro-and nanoscale deformation measurement of surface and internal planes via digital image correlation. Experimental Mechanics. 2007;47(1):51-62.
[7] Mehdikhani M, Aravand M, Sabuncuoglu B, Callens MG, Lomov SV, Gorbatikh L. Full-field strain measurements at the micro-scale in fiber-reinforced composites using digital image correlation. Composite Structures. 2016;140:192-201.
[8] Pettolino FA, Walsh C, Fincher GB, Bacic A. Determining the polysaccharide composition of plant cell walls. Nature protocols. 2012;7(9):1590-607.
[9] A. Sluiter BH, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, and D. Crocker. Determination of Structural Carbohydrates and Lignin in Biomass. National Renewable Energy Laboratory. 2012;NREL/TP-510-42618. National Renewable Energy Laboratories.
[10] Fuentes C, Willekens P, Petit J, Thouminot C, Müssig J, Trindade L, et al. Effect of the middle lamella biochemical composition on the non-linear behaviour of technical fibres of hemp under tensile loading using strain mapping. Composites Part A: Applied Science and Manufacturing. 2017;101:529-42.