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Multi-scale analysis of the structure and mechanical performance of woody hemp core and the dependence on the sampling location

Johnny Beaugrand[a,b,*], Mélanie Nottez[c], Johannes Konnerth[d], Alain Bourmaud[e]

[a] INRA, UMR614 Fractionnement des AgroRessources et Environnement, F-51100 Reims, France
[b] Université de Reims Champagne-Ardenne, UMR614 Fractionnement des AgroRessources et Environnement, F-51100 Reims, France
[c] Mines Douai, Polymers and Composites Technology & Mechanical Engineering Department, Douai, France
[d] BOKU – University of Natural Resources and Life Sciences – Vienna, Department of Material Sciences and Process Engineering, Institute of Wood Technology and Renewable Resources, Konrad Lorenz Straße 24, A-3430 Tulln, Austria
[e] LIMAT b, Université de Bretagne Sud, Rue de Saint Maudé, 56321 Lorient Cedex, France

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ABSTRACT

A multi-scale length and multi-feature exploration of woody hemp core (WHC) using 6 internodes (INs) along the height of the stem was conducted, and then, the putative IN location dependence of composites made of the WHC was evaluated. At the nanoscale level, we observed a good inter-stem reproducibility of cell wall properties using nanoindentation tests as well as moderate increases in the values of the indentation modulus and hardness from the bottom to top of the stem (8.5–10.5 GPa and 200–350 MPa, respectively). Biochemical analysis revealed that the lignin content decreased significantly (by approximately 1.5% in terms of the WHC dry matter mass) from the bottom to the top of the stem. Individual stem carbohydrate trends differed when compared with the average values of a group of 10 stems. Along the height of the stem, no variation in the total carbohydrate content was observed in the average of 10 stems, but the monosaccharide details exhibited mixed behaviors. The arabinose and galactose contents increased from the bottom to top of the stem and were strongly correlated with structural properties, i.e., relative density, Young's modulus, and toughness, as well as with lignin content. At the microscale level, from the bottom to top IN of the stems, the relative density of the WHC exhibits a 2.8-fold reduction. At the mesoscale level, bending tests showed huge variations between IN locations; Young's modulus, strength at break and fracture energy exhibit 4, 2 and 5-fold variations, respectively. Despite all of these structural and biochemical variations along the WHC stem, composites made of particles from the bottom, median, or top WHC locations did not show any variations in Young's modulus, stress or elongation at break. The influence of the extrusion and injection process steps of making wood–plastic composites is discussed in connection with the preservation of the pre-processing intrinsic potential of the raw fiber materials.

1. Introduction

In recent years, many studies and industrial efforts have addressed the integration of plant fibers as a composite polymer reinforcement. The most interesting fibers found in Europe are flax and hemp fibers due to their good performance regarding specific mechanical properties (Placet, 2009; Bourmaud et al., 2010; Beaugrand and Berzin, 2013), their environmental and ecological benefits (Pervaiz and Sain, 2003; Joshi et al., 2004; Le Duigou et al., 2011), and their low cost.

From economic and environmental perspectives, it is interesting to study the use of plant co-products to avoid the use of new agricultural lands, to limit competition with alimentary products, and to ensure several sources of remuneration to farmers. In the case of oleaginous flax, it was shown that in addition to seeds and shives, the sclerenchyma fibers could be valorized as a polymer reinforcement due to their mechanical performance (Pillin et al., 2011). Hemp fibers exhibited potential as a composite (Bourmaud and Baley, 2007; Hu and Lim, 2007; Beckermann and Pickering, 2008; Sawpan et al., 2011) reinforcement because of their specific mechanical properties (Dai and Fan, 2010; Duval et al., 2011; Placet

Abbreviations: CV, coefficient of variation; IN(s), internode(s); NI, nanoindentation; WHC, woody hemp core.

* Corresponding author at: INRA, UMR614 Fractionnement des AgroRessources et Environnement, F-51100 Reims, France. Tel.: +33 3 26913822.
E-mail address: johnny.beaugrand@reims.inra.fr (J. Beaugrand).

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et al., 2012); however the potential of plant co-products, such as woody pieces, as composite reinforcements remains unclear.

Hemp is an annual plant consisting of non-wood material. However, after decortication of the stems, two products are obtained: the long, well-known sclerenchymatic bast fibers of meristematic origin, which are mainly used for reinforcement, and the 'short' xylem fiber corresponding to the woody core of the stem (approximately 70% of the stem mass), which has a tissular organization similar to that found in hardwood. In this paper, we focus on the latter, an agro-industrial co-product. Other studies have used woody hemp core (WHC; also called stalk fiber, chenevotte, hemp hurd, or shives) to modify MgO-cement (Stevulova et al., 2012; Števulová et al., 2012) in building engineering; these studies found that despite its high lignin content, WHC could be extracted from the entire plant by a steam explosion process (Vignon et al., 1995).

WHC that is not decorticated from the plant stem has an interesting yield of ethanol, biogas, heat, and electricity (Kreuger et al., 2011; Barta et al., 2013) production. Raw WHC was recently used in a thermoplastic composite as a reinforcement agent for a starch-based biopolymer (Lopez et al., 2012). The mechanical properties reported for WHC in previous studies may fulfill some technical requirements. A final illustration of the application of WHC in composites is the styrene–butadiene rubber composites presented by Wang et al. (2011). The authors reported that the mechanical properties of the composite improved with an increasing content of WHC powder, and interestingly, the short WHC fibers had a positive effect on the elongation at break compared with results obtained for long fibers (i.e., bast fibers).

Compared with flax, hemp bast fibers exhibit a relatively low Young's modulus and tensile strength at break and have a large dispersion for these two properties. This variability, which could be due to morphological and structural parameters, particularly the lumen size (Placet et al., 2012), of the mechanical properties could be problematic in industrial settings. In a recent work (Marrot et al., 2013), we partially explained this scattering using a morphological analysis of the stem that exhibited heterogeneous fiber sections. In addition, many parameters influence the mechanical properties of natural fibers, including WHC variety, surrounding growth conditions (e.g., input, water, seedling rate), decorticating process, surrounding testing conditions (humidity, temperature), position of the fiber in the stem (Charlet et al., 2007; Duval et al., 2011), fiber biochemical composition (Alix et al., 2008), fiber diameter (Baley, 2002), and fiber microfibril angle (Bourmaud et al., 2013b). The effects of these numerous parameters could explain the variation in Young's modulus and tensile strength from one batch to another and within one batch. Moreover, although it is less applicable to hemp than to flax, the degree of retting could also be an important factor (Nykter et al., 2008).

The location of the fiber in the stem could impact the mechanical properties of the fiber (Duval et al., 2011). The impact of this parameter on the mechanical performance, density, and carbohydrate composition of WHC is questionable. In the case of hemp bast fiber, a correlation between the structural pectins and matrix pectins of the S2 layer was observed compared to the behavior in flax (Marrot et al., 2013). From an industrial perspective, this correlation must be explored to quantify the influence of the reinforcement properties on the properties of the final composites. In the case of flax, a correlation between the mechanical properties of the elementary fibers and the composite performance was highlighted with a polypropylene (PP) matrix (Martin et al., 2013).

Tensile tests are typically used to determine the mechanical properties of plant fibers. This study focuses on WHC; the procurement of suitable samples of WHC for tensile experiments could be problematic due to its heterogeneous structure. A bending test was successfully performed in recent years due to the flexible parallelepiped geometry of WHC (Bag et al., 2012). Another method of estimating the stiffness of a material is the nanoindentation (NI) test. In previous works (Bourmaud and Baley, 2012; Alix et al., 2012), we demonstrated the significance of NI in the fine characterization of vegetal fiber cell walls. NI exhibited considerable potential for in situ and comparative analyses without any handling or sampling; the use of NI on plant cell walls allows local mechanical information about the different constituent layers to be obtained. The average NI modulus of fibers tested in the longitudinal direction is low compared to the modulus obtained with conventional tensile tests (Gindl et al., 2008; Bourmaud and Baley, 2010), but the scales and solicitation modes differ considerably. The wall is loaded at an angle of approximately 25° based on the face angle of the Berkovich-type indenter. Thus, the resulting three-dimensional stress is a result of the deformations and thus the modulus in the longitudinal direction and is also affected by the transverse and shear moduli (together the microfibril angle and Poisson ratio) (Jäger et al., 2011a). Therefore, the longitudinal modulus of anisotropic natural tissues, such as wood or plants, cannot be derived directly using NI tests except in cases where special test setups are used (Jäger et al., 2011b) that induce an underestimation of the longitudinal modulus. Nevertheless, NI allows pertinent comparative measurements to be performed. In a previous work, we demonstrated the use of NI in in situ investigations of the flax stem, sclerenchyma fibers, and woody core of the plant. NI has also been used in comparative studies of hairs (Wei et al., 2005; Wei and Bhushan, 2006), wood (Gindl and Schöberl, 2004; Tze et al., 2007), and bamboo cell walls (Yu et al., 2007). Nanoindentation could also be used to estimate plant cell walls nanomechanical properties for numerical models feeding (Gershon et al., 2010; Haldar et al., 2011).

This paper has three interrelated objectives. The first objective is to evaluate whether significant variations in carbohydrate or lignin content or in structural properties are present in WHC in different areas along the hemp stem; thus, density measurements, flexural tests, and biochemical analyses were carried out on various INs in the WHC. The second objective is to quantify the impact of localization in the stem on the micromechanical properties of the WHC cell walls. NI measurements were conducted for this purpose. The third and final objective is related to the first two. If the multi-scale analysis of the structure indicates a dependence on the sampling location, the presence of a functional impact on composite properties was investigated. For this purpose, we prepared and investigated composites made from distinct WHC sample locations.

2. Materials and methods

2.1. Plant material and sampling

Hemp plants (*Cannabis sativa*, variety Fedora 17, monoicous plants) were supplied by Fibres Recherches Développement® (Troyes, France) and were grown in one field in Aube (France) in 2009. Ten vigorous stems measuring approximately 2 m each were chosen. The stems were measured and cut close to the nodes using a cutter, and only the IN parts were kept for our investigation. Nodes that were a few centimeters long were not considered. The peripheries of the stem INs containing the long fibers (bast fibers) were manually removed to retain only the woody part. The decorticated WHC tubes were then cut into two parts along the long axis. One part was used in the density measurements, the NI tests, and the three-point bending tests on the calibrated sticks. The remaining materials and the second part of the decorticated WHC tubes were used in both the biochemical analysis and the formation of compounds for the mechanical evaluation of composites.

For the inter-plant variability assessment, we compared the contents of each similar IN location from 1 to 6 (called IN-1–IN-6) on the 10 plants in the group. For the intra-stem variability evaluation,