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Analysis of the hemp fiber mechanical properties and their scattering (Fedora 17)

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ABSTRACT

Understanding the mechanical behavior of plant fibers is a key to their development in composite reinforcement. The aim of this work is to better understand the low and scattered mechanical properties of hemp fibers (Fedora 17 variety) by highlighting innovating elements about the relationship between the cell wall components and the fiber mechanical performances. In first time, the morphology of hemp fibers within the stem is studied. Significant differences of lumen or fiber size is noted according to their location. Then, the biochemical analysis, despite a cellulose rate similar to flax varieties, highlights important differences for the nonstructural and matrix pectins distribution and quantity compared with flax. For the first time for hemp, nanoindentation investigations carried out *in-situ* on stems show that, no matter the location in the stem, the mechanical properties of the S2 layer were similar, proving a good reproducibility of the cell walls structure. Despite moderate differences between the crystallinity indexes, the X-ray diffraction patterns highlight the presence of a significant amorphous matrix polymer rate in the case of hemp.

1. Introduction

Natural fibers are increasingly seen as a good reinforcement material in polymeric matrix composites. They can compete with glass fibers, thanks to their good specific mechanical properties (Bourmaud et al., 2010; Duval et al., 2011) due to their low density (Aziz and Ansell, 2004), their relatively low cost (Dittenber and Gangarao, 2012) and their biodegradability (Stamboulis et al., 2001). However, their wide-spread physical and mechanical properties (Duval et al., 2011; Pillin et al., 2011) make the natural fibers difficult to use for structural applications when high reliability is required (Pomel et al., 2003; Stamboulis et al., 2001). In Europe, hemp and flax are easily available and could be considered as attractive candidates to replace glass fibers in composites. Therefore, hemp fibers are of interest due to their specific mechanical properties and their price, which has been cheaper and more constant over the years than those of flax (Nova Institute, 2012).

Hemp has been less studied than flax and its morphology and mechanical behavior are far from being fully understood. In the case of hemp, the fibers used for polymer reinforcement originate from primary cells located in the primary phloem (Gorshkova et al., 2012) at the stem periphery and are associated through their pectic middle lamella to form bundles of several dozens of fibers (Crônier et al., 2005). These primary fibers could reach a length between 5 mm and 100 mm and unlike flax fibers, hemp shows great variations in fiber diameters which could vary between 15–40 μm (Crônier et al., 2005; Garcia et al., 1998; Sankari, 2000). Unlike flax, hemp is characterized by the existence of a secondary fiber network; these secondary xylem fibers (Chernova and Gorshkova, 2007) are shorter (around 2 mm) and thinner (6 μm) than the primary fibers (Crônier et al., 2005; Sankari, 2000) and represent around 10% of the total bast fibers (Crônier et al., 2005). They are not systematically present in the stem. According to Sankari (2000), the secondary fibers seems to be more abundant in female plants and, when they are present, they are more likely located in the

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bottom of the stem and their proportion decreases from the bottom to the top (Abot, 2010). However, cultivated hemp varieties in France are mainly monoecious, which means that they have male and female flowers on the same plant: the sexual distinction is no longer possible.

As reported for flax (Baley, 2002), hemp fiber consists of a succession of concentric cylinders with a small channel in the middle called lumen. The outer cell wall designed as the primary cell wall is thin (only 0.1 or 0.2 μm thick (Bos and Donald, 1999; Thygesen et al., 2006)). The secondary cell wall is made of three layers (S1–S3). The main layer, representing around 80% of the total section, is the S2 layer, constituted of highly crystalline cellulose fibrils spirally wound in a matrix of amorphous hemicelluloses and pectins (Crônier et al., 2005; Goubet et al., 1995). The cellulose fibrils make a 10–11° angle with the axis of the fiber (Bledzki and Gassan, 1999; Placet et al., 2011) - which is called micro-fibrillar angle (MFA). The secondary wall is characterized by the presence of highly crystalline cellulose; the structure of hemp cellulose is considered to be intermediate between the highly crystalline cellulose of flax (Kalia and Kaith, 2008) and the semi crystalline one in kenaf (Bonatti et al., 2004). Many authors investigated the crystallinity of hemp fibers by using X-ray diffraction (Dai and Fan, 2010; Le Troedec et al., 2008; Li and Pickering, 2008; Li et al., 2009; Wang et al., 2007). The results show a percentage of crystallinity between 56% and 80%.

The biochemical composition of natural fiber cell walls is known to have an influence on their mechanical properties (Morvan et al., 2003). Cellulose is the component with the highest Young's modulus (Kroon-Batenburg et al., 1986; Salmén, 2004). It is one of the crucial elements to guaranty the rigidity of the fiber. Moreover, the fiber rigidity will depend on the ratio between structural and matrix pectins. Alix et al. (2009) noted higher mechanical performances for Hermes flax (Young's modulus of 68 ± 36 GPa for Hermes, and 38 ± 13 GPa for Oliver; tensile strength of 1450 ± 840 MPa for Hermes, and 720 ± 290 MPa for Oliver), correlated to the cellulose rates of the two varieties (84 ± 3.5% for Hermes, and 77 ± 2.5% for Oliver). They explained this phenomenon by the inter-fibrillar distances (lower for Hermes) due to lower amount of non-cellulosic polymer matrix between these cellulose fibrils. In the case of Hermes flax, the presence of glucomannan bridges could explain part of the stiffness differences.

Compared with flax, hemp shows relatively low Young's modulus, tensile strength at break, and a large scattering for these two properties. Little data is given in the literature, some are reported in Table 1. Values reported by Placet (2009) are particularly low. Nevertheless, this author highlighted that the rigidity of the fiber is improved by a factor of 1.32 at 25 °C after stress cycles thanks to an accommodation phenomenon. An interesting correlation between tensile properties and fiber diameters was noticed by several authors (Duval et al., 2011; Fan, 2010; Placet et al., 2012); the smaller the diameter, the higher the Young's modulus and the ultimate strength. This phenomenon is generally explained by the fact that fibers break in regions where their diameter is higher due to a higher probability of containing defects, which may lead to break.

Most of the time, tensile tests are used to determine the mechanical properties of a fiber. Another way to estimate the stiffness of a material is the nanoindentation test. In previous works (Alix et al., 2012; Bourmaud and Pimbert, 2008; Bourmaud and Baley, 2009, 2010, 2012), we showed the significance of the nanoindentation for the fine characterization of vegetal fiber cell walls. The nanoindentation showed a considerable potential for *in-situ* and comparative analysis without any handling or sampling; thus, by using nanoindentation on plant cell walls, it is possible to obtain local mechanical information from the different constituting layers. The average longitudinal modulus of fibers from nanoindentation experiments is low compared to the modulus obtained with conventional tensile tests (Bourmaud and Baley, 2010; Gindl et al., 2008), but the scales and the solicitation modes are very different. Because of face angle of the Berkovich-type indenter, the wall is loaded at an angle of approximately 25°. Consequently, the resulting three-dimensional stress is not only governed by the longitudinal modulus, but also affected by the transverse modulus, inducing an underestimation of the longitudinal modulus. Nevertheless, nanoindentation makes it possible to carry out pertinent comparative measurements.

The aim of this article is to better understand the origin of the relatively weak hemp fiber mechanical properties, as well as why they are scattered. We propose an original study through, for the first time on hemp stem, *in-situ* nanoindentation, analysis of the fiber morphology and finally, a study of the relationship between the fibers biochemical composition and their mechanical performances. In first time, we analyzed the fibers morphologies; thin cuts of the same hemp stem sections were observed by using electronic and optical microscopy. Furthermore, the biochemical composition of the cell walls was determined to better understand the tensile mechanical properties. Lastly, in order to investigate the origin of the fiber stiffness spreading, *in-situ* measurements of rigidity were carried out on the hemp stems by using nanoindentation and X-ray diffraction (XRD) analysis were conducted to compare fiber hemp crystallinity with those of well-known flax varieties. Finally, tensile tests were performed on manually extracted single hemp fibers to highlight the hemp mechanical properties and compare them with the literature data.

2. Experimental

2.1. Materials

Hemp plants (*Cannabis Sativa* L, variety Fedora 17) used for this study were supplied by the Kerbastic Domain (Guidel, France), where they were grown in 2011. They were harvested in September. To have several tensile references, two other hemp batches have been used. They were supplied by the LCDA company (Aube, France), in 2007 (Fedora 17 variety) and 2009 (Felina 32 variety).

Before extraction, in order to improve their handling, each piece of the stem was soaked in water for 72 h (Bourmaud et al., 2010), which ensures a relatively good separation of fibers and washes their surface from impurities. This soft treatment makes the extraction easier without any damage or biochemical structure modification. The fibers were then removed from the middle of the stem, since it has been shown that fibers from this area bring the best properties (Charlet et al., 2007; Duval et al., 2011).

In addition to hemp, flax fibers were also used for XRD analysis. Oliver (oleaginous variety) and Hermes (Textile variety) flax fibers were harvested in North-West of France in 2003. The flax fibers were laid in the field for drying for 4 weeks after harvesting to allow for dew-retting that is the development of fungi within the stem, which degrades their middle lamellae and further facilitates the extraction of the fibers.

2.2. Sample preparation for morphological analysis and nanoindentation experiments

A hemp stem was embedded in LR-White resin as previously described (Andème-Onzighi et al., 2000). Its surface topography was minimized by using an ultramicrotomic apparatus. The sections obtained were stained for observation with a transmission optical microscope. The average surface roughness, Ra, was measured by using atomic force microscopy (AFM) experimentation. The roughness measurements were made using the microscope's section analysis software (V5.12r3 by Digital Instruments) and