Extraction and Characterization of Fibers from Palm Tree

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The characterization of fibers extracted from leaflet, the empty fruit bunches, leaf sheath, and spath of palm tree was performed. The fibers were extracted using three different procedures through chemical and /or enzymatic methods. The raw fibers studied have xylose contents between 13-22% and glucose content between 30% and 45%. The microfibrillar angle (MFA) values are in the order: bunch > spath > leaf sheath >> leaflet. Spath and leaf sheath, which naturally occur in a woven form present poor mechanical strength but could be readily used to produce cheap composites. Leaflet fibers extracted from date palm tree exhibiting a low MFA (16°), a high cellulose content, and cellulose crystallinity present the highest ultimate tensile strengths (≈ 1250 $N.mm^{-2}$).

Keywords: Palm tree; Fibers; Crystallinity; Microfibrillar angle; Tensile strengths

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INTRODUCTION

Synthetic fibers, because of their high stiffness and strength, are widely used in the textile industry as well as in composites. However, these fibers show some disadvantages in terms of biodegradability, processing costs, recyclability, energy consumption, and machine abrasion. Thus there has been an increased interest in production and use of natural fibers for textiles and composites. Natural fibers have accompanied human societies since prehistoric times. However, during the 20th century, the production of cheap petroleum-based fibers has nearly destroyed the production and utilization of natural fibers such as hemp and flax in the western countries. Recently, environmental concerns and the growing global waste problem have spurred much research into the development of bio-based materials and motivated governments to increase the legislation pressure.

The advantages of plant fibers over synthetic ones include their low cost, light weight, local availability, and their outstanding mechanical properties (Bismarck *et al.* 2005). Basically, a natural fiber is composed of rigid crystalline cellulose microfibrils embedded in an amorphous matrix of lignin and hemicelluloses. In most plant fibers, the cellulose microfibrils are at an angle to the cell axis called the microfibrillar angle (MFA). MFA is considered as a key factor to explain the mechanical properties of fibers, especially their stiffness. A lower MFA means the cellulose microfibrils are well oriented along the fiber axis and therefore these fibers will have relatively lower elongations (Reddy and Yang 2007). The chemical composition (in terms of cellulose, lignin, and hemicelluloses), MFA,

as well as the crystallinity index (CrI) of the cellulose are structural parameters that vary from a plant fiber to another and are important variables that determine the overall properties of the fibers. As a result, natural fibers exhibit a very large variation as a function of the species. Moreover, the procedures used for the extraction of the fine fibers from the bast (retting) greatly impact the properties of the fibers (Tahri 2011). As a consequence, the availability of natural fibers with the required quality for textile and composite industries is an important issue to fulfill the demand. Chemical retting (dilute solution of NaOH, Amel *et al.* 2013) and enzymatic retting (using pectinase, Akin *et al.* 2001; Dodd and Akin 2005) have been reported to produce fibers at the lab scale. Ultrasonic processing eventually coupled to chemical methods also appears as a promising way (Renouard *et al.* 2014).

Date palm tree (*Phoenix dactylifera* L.) plays a central role in the economy of North Africa and Middle East countries (Botes and Zaid 2002; Janick *et al.* 2008; El-Deek *et al.* 2010), and palm co-products have been identified as an important contributor of biomass in this part of the world. Every year during the date harvest, around 2 million tons of dry palm fronds are produced. (Klein and Zaid 2002; Genin *et al.* 2004; FAO 2011). There are many parts of the date palm tree from which fibers could be extracted. Nevertheless, data available on the chemical composition and the mechanical properties of these fibers are poor or incomplete (Satyanarayana *et al.* 1986, 1982; Sreekala *et al.* 1997). Prior knowledge regarding these fibers is essential for evaluation of their potential for different applications. In this short paper we describe the characterization of fibers extracted from various parts of date palm tree. Fibers from dwarf palm leaflet were also studied for comparison. The fibers were extracted using three different procedures (through chemical and /or enzymatic methods) and characterized in terms of cellulose, hemicelluloses, lignin contents, CrI, and MFA of cellulose and ultimate tensile strengths.

EXPERIMENTAL

Feedstock and Chemicals

Fibers from date palm tree (*Phoenix dactylifera* L.*)* and dwarf palm tree (*Chamaerops humilis*) were collected in spring 2015 in Elmanar II garden in Tunis city. Fucose, glucose, xylose, galactose, mannose, rhamnose, arabinose, and galacturonic acid, as well as glucuronic acid used as standard for chromatography were provided by Sigma-Aldrich. Viscozyme® is commercially available (Novozymes) and described in enzyme-retting formulation (Akin, 2001). This multi-enzyme complex contains a wide range of carbohydrases (cellulase and hemicellulase).

Chemical Characterization

Klason lignin procedure (acid insoluble residues determination)

Extractive-free samples were ground, and their moisture content was measured (Kern MRS 120-3 moisture analyzer). Approximately 0.175 g (exactly weighed) of dried samples were weighed and put in centrifuge tubes (50 mL tubes from Corning®); 1.5 mL of sulfuric acid (72 %) were added, and then the mixture was stirred few times with a glass rod and placed in a water bath at 30 °C for 1 h. After adding 42 mL of pure water, the tubes were placed in an autoclave set at 121°C for 1 h. The samples were then cooled and filter with glass microfibers (particle retention 1.2 µm). The insoluble residue was washed with pure water, dried in a 105 °C oven, and then weighed. The soluble fraction was recovered

and completed up to 100 mL with water and then analyzed by high performance anion exchange chromatography combined with pulse amperometric detection (HPAE-PAD).

HPAE-PAD analyses

Monosaccharide contents of the soluble fraction were analyzed by HAPE-PAD (ICS-3000 Dionex) equipped with a Dionex CarboPacTM PA-20 (3x150 mm) analytical column. Filtered samples (20 µL) were eluted at 35 °C and at 0.4 mL/min with the following composition: pure water 99.2% /250 mM NaOH 0.8% : 0 to 20 min ; pure water 75%/250 mM NaOH 20% /NaOAc (1 M) - NaOH (20 mM) 5% 20 to 37 min ; pure water 40% /250 mM NaOH 20%/NaOAc (1 M) - NaOH (20 mM) 40% 37 to 41 min. Each elution was followed by a wash and subsequent equilibration time. External sugar and uronic acids standards were used for calibration (7 points per curve).

CrI and MFA

An X-ray diffractometer from Oxford diffraction (Supernova model) was used to estimate the cellulose structural parameters. The Supernova system consists of a kappa geometry, four circle goniometry for sample orientation with a detector arm, a CCD area detector delivering a digitized signal to 18-bit resolution and an X-ray tube, with a copper source, the nominal point of which is at 50 keV/1 mA. For both crystallinity index and MFA analysis the samples were oven-dried before analysis. For crystallinity index determination, the powder was made from the samples for MFA samples, and the measurement were made on oriented group of fibres.

Crystallinity index

The diffractogram was extracted from experimental data at a 2θ angle between 5° and 40° with a step of 0.05°. The crystallinity index (CrI) was determined as the percentage of crystalline material in biomass according to Eq. 1 (Segal *et al.* 1959),

$$CrI = \frac{(I_{002} - I_{am})}{I_{002}} \times 100 \quad (1)$$

where CrI is the relative degree of crystallinity, I_{002} is the intensity of the diffraction from the 002 plane at $2\theta = 22.5°$, and I_{am} is the intensity of the background scatter at $2\theta = 18.7$.

Microfibril angle

Parameter *T* defined by Cave (1966) was graphically derived from the diffraction pattern. This pattern consists of the 002 arc intensity extracted at the circle along 2θ angle integrated around 22.4°. The average MFA of each sample was estimated using Cave's formula: MFA = 0.6×*T*.

Ultimate Tensile Strengths

Test specimens were first manually separate and stored in a conditioning chamber controlled temperature of 20 ± 1.5 °C and a relative humidity of 60 ± 1%, for 24 h. The tensile strength testing of fiber was carried out on an FAVIMAT +, and 30 elementary fibres were tested at a constant speed of 5 mm/min in accordance with XP T 25-501 – 3. The tests were performed using a load cell of 3200 cN; the clamping length was 10 mm.

The effective cross-sectional area was calculated from scanning electron microscopy (SEM), using a Hitachi 3000 instrument. All images were taken at an

accelerating voltage of 15 kV. The sample surfaces were coated with a thin layer of gold using a Sputter Coater SC7610 to provide electrical conductivity (see the Appendix).

RESULTS AND DISCUSSION

Fibres were extracted from different parts of the palm tree: the leaflet, the empty fruit bunch, the spath which is a fibrous membrane wrapping the fruit bunch and the leaf sheath which is the basal part of the leaf that encircles the stem. Regarding spath and leaf sheath, they naturally occur in the plant already in woven form. These materials could be readily impregnated with a polymer or another matrix to produce cheap composites.

The chemical compositions in terms of glucans (mainly cellulose), xylans (from hemicelluloses), and acid insoluble residues (AIR) of the raw materials used in this study are given in the Table 1. The AIR is determined using the Klason lignin procedure and is mainly composed of lignin but tannins, proteins and inorganics are also recovered in this fraction. AIR was relatively important in the leaflet, it accounted for 32% and 36% of the whole leaflet from date palm and dwarf palm tree respectively. High lignin contents were already reported for the leaf of Indian palm trees (42% of palmyrah palm tree and 28% for talipot palm tree, Satyanarayana *et al*. 1986).

The spath displayed a high cellulose content (≈ 45% of glucans) and all the raw fibers studied have a high xylose (13 to 22%) content, which is usual in monocotyledon plants. The cellulose crystallinities were determined through X-ray diffraction. Leaflets and bunch displayed a substantial higher crystallinity (≈ 50%) compared to spath and leaf sheath. SEM images and cross sectional area of the technical fibers are given in the Appendix.

Retting is the process for removing non-cellulosic material attached to the fibers to release individual fibers. In this study, based on literature data (Akin 2001; Amel *et al*. 2013; Renouard 2014), three different processes were experimented:

- conditions 1 = NaOH 5% in water,
- conditions 2 = NaOH 1% in water and ultrasound,
- conditions 3 = enzymatic treatment followed by NaOH 1% in water and ultrasound.

Taking into account the high xylose content (15 to 22 %) and the low proportion pectic compounds in the raw materials (<5%, data not shown), an enzyme complex with a high hemicellulase activity (viscozyme ®) was selected.

Table 1. Chemical Composition and Crystallinity Index of Raw and Retted Fibers

		Spath[a]	Bunch[a]	Sheath[a]	Leaflet 1[a]	Leaflet 2[b]
Raw Fibers	Glc[c]	44.7	37.0	34.2	38.5	29.7
	Xyl[d]	22.5	18.4	16.7	13.0	14.9
	Other sugars[e]	14.5	17.6	7.7	9.8	14.9
	AIR[f]	16.8	26.5	36.3	32.0	36.3
	CrI[g]	42.8	48.8	35.5	52.8	46.3
Retted fibers : Conditions 1 NaOH 5%	Glc[c]	35.6	45.4	56.0	42.0	36.8
	Xyl[d]	16.5	22.6	11.8	13.0	14.6
	Other sugars[e]	10.4	14.7	7.18	6.4	9.8
	AIR[f]	32.2	18.1	19.2	22.6	23.9
	CrI[g]	33.6	48.8	nd	50.0	41.6
Retted fibers : Conditions 2 NaOH 1%, US	Glc[c]	47.0	43.6	41.6	45.0	47.2
	Xyl[d]	24.0	24.6	16.5	13.4	17.5
	Other sugars[e]	11.4	15.6	6.6	4.6	9.2
	AIR[f]	17.3	16.0	29.7	31.3	22.6
	CrI[g]	nd	nd	37.6	51.9	43.6
Retted fibers : Conditions 3 NaOH 1%, US, enzyme	Glc[c]	38.8	25.5	42.4	48.7	41.0
	Xyl[d]	19.0	22.0	16.6	14.7	17.7
	Other sugars[e]	12.6	10.4	8.2	6.9	9.2
	AIR[f]	19.6	19.2	26.8	24.2	23.5

[a] from date palm tree ; [b] from dwarf palm tree ; [c]Glucose ; [d]Xylose ; [e]Mannose, galactose, arabinose ; [f]Acid Insoluble Residue ; [g]Crystallinity Index

Using conditions 1 (5% NaOH), for the bunch, leaf sheath and leaflet, we observed a decrease of the AIR associated with an increase in the glucans content justified by extensive delignification. A substantial increase of the crystallinity of cellulose was also observed. However for the spath fibers, a decrease of the sugars content and of the crystallinity suggested that the harsh basic conditions used provoked an important decrease of the cellulose crystallinity through alkaline hydrolysis and peeling mechanisms. On the other hand, under conditions 2, an increase of the cellulose content was observed for all the fibers. These milder conditions also caused a slight delignification and prevented the degradation of the xylans polysaccharides and the cellulose crystallinity. Using a combination of chemical and enzymatical retting methods (conditions 3) with spath and bunch, the important decrease of the glucans content (compared to conditions 2) demonstrated the cellulase activity of the enzymatic cocktail. Regarding leaf sheath and leaflet from date palm tree (leaflet 1), sugars were not affected, whereas a higher delignification was observed. Despite a low impact of the enzymatic hydrolysis on the fiber composition in cellulose and xylans, the enzyme could disrupt the remaining polymers sufficiently (through a weakening of the lignin-hemicellulose complex) to enhance the removal of lignin by NaOH. A similar enzymatic weakening of a

lignocellulosic matrix was already described before an organosolv delignification (Obama 2012).

In most plant fibers, the cellulose microfibrils are oriented at an angle to the cell axis called the microfibrillar angle (MFA). The MFA is a characteristic value that varies among plants. In general, the tensile strength increases as the MFA value decreases and as the cellulose content increases. The MFAs of the raw fibers were determined through X-ray diffraction, and the angles are given in Table 2. The MFA values were in the following order: bunch > spath > leaf sheath >> leaflet. Large MFA values were found for fibers from spath, bunch, and leaf sheath (28-37°). MFA of the same order of magnitude were described for coir (Trana *et al.* 2015), oil palm empty fruit bunch (Bismarck *et al.* 2005), and fibers from coconut tree (Satyanarayana 1982). On the other hand, fibers from leaflets have a low MFA (<20°), close to sisal (Bismarck *et al.* 2005) and to jacitara palm (Fonseca *et al.* 2013).

Ultimate tensile strengths (in N/mm^2) and modulus of elasticity (MOE) of the fibers extracted using conditions 3 were determined, and an important discrepancy was observed (Table 2). Leaf sheath fibers, despite a relative high cellulose content, display poor mechanical properties. As previously described, it can be seen that the observed ultimate tensile strength of the fibers seem to depend largely on microfibrillar angle; generally the lower MFA, the higher will be the strength. Leaflets extracted from date palm exhibited the lowest MFA, higher cellulose content and crystallinity, and the highest ultimate tensile strengths.

Table 2. Fibers strength, MOE, and Microfibrillar Angle

	Spath[a]	Bunch[a]	Sheath[a]	Leaflet1[a]	Leaflet2[b]
Strength[c], N/mm^2	397.2 ± 112.6	573.0 ± 86.4	215.8 ± 80.0	1246.7 ± 444.7	490.4 ± 148.1
MOE (GPa)	1.1±0.7	6.9±1.8	5.1±1.3	26.1±11.2	10.1±1.9
MFA (d°)	30.2	36.8	27.8	16.0	18.8

[a] from date palm tree ; [b] from dwarf palm tree ; [c] determined from the fibers after retting with (NaOH 1%, US, enzyme) ; [c] determined from the raw fibers.

Taking into account the characteristics presented by palm tree fibers, it may be assumed that palm tree is a potential source of natural fibers for the conception of green composites and new materials for different applications.

CONCLUSIONS

1. Fibers were extracted from leaflet, empty fruit bunch, leaf sheath, and spath of palm tree using chemical and/or enzymatic methods.
2. Raw and retted fibers were characterized in terms of cellulose, hemicelluloses, lignin contents, CrI, and MFA of cellulose and ultimate tensile strengths.
3. Leaflet fibers extracted from date palm tree, which exhibiting a low MFA (16°), a high cellulose content, and a cellulose crystallinity, presented the highest ultimate tensile strengths.

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APPENDIX

Cross-sectional Area Determination

The effective cross-sectional area was calculated from scanning electron microscopy (SEM); the instrument was a Hitachi 3000. All images were taken at an accelerating voltage of 15 kV. The sample surfaces were coated with a thin layer of gold on the surface using a Sputter Coater SC7610 to provide electrical conductivity.

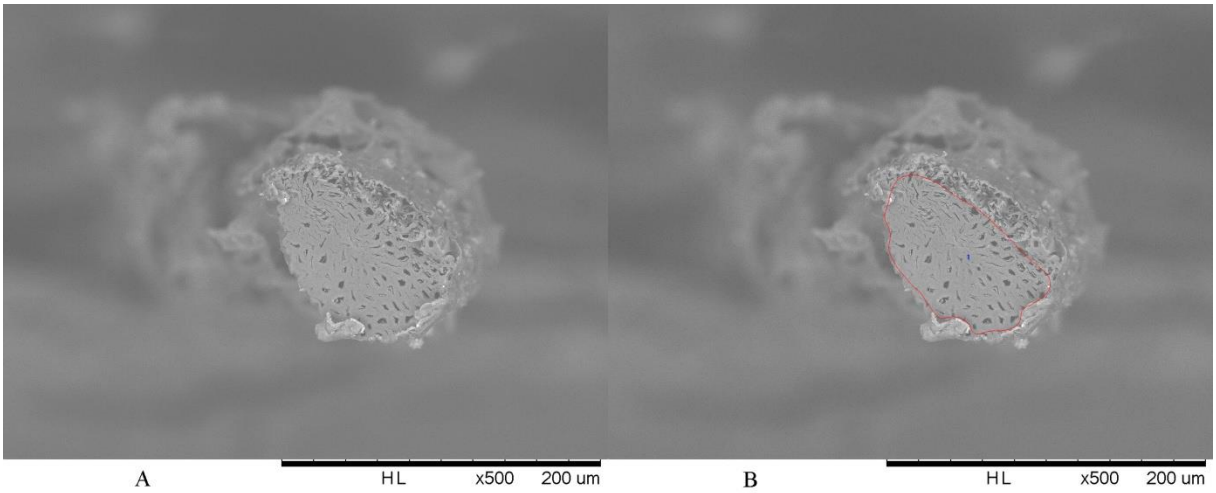

Fig. X: A) Fiber-cell microstructure: cross-section view showing the fiber-cells, lumens and middle lamellae **B)** effective cross-sectional area

Table X. Fibers Cross Section Area Determined from SEM Pictures

	Spath[a]	Sheath[a]	Bunch[a]	Leaflet1[a]	Leaflet2[b]
Cross-section (μm^2)	23001,9±2484.6	3166.1±340.9	3374.1±504.1	18126.1±321.9	2970.2±513.3

[a] from date palm tree ; [b] from dwarf palm tree

Morphological Characterization

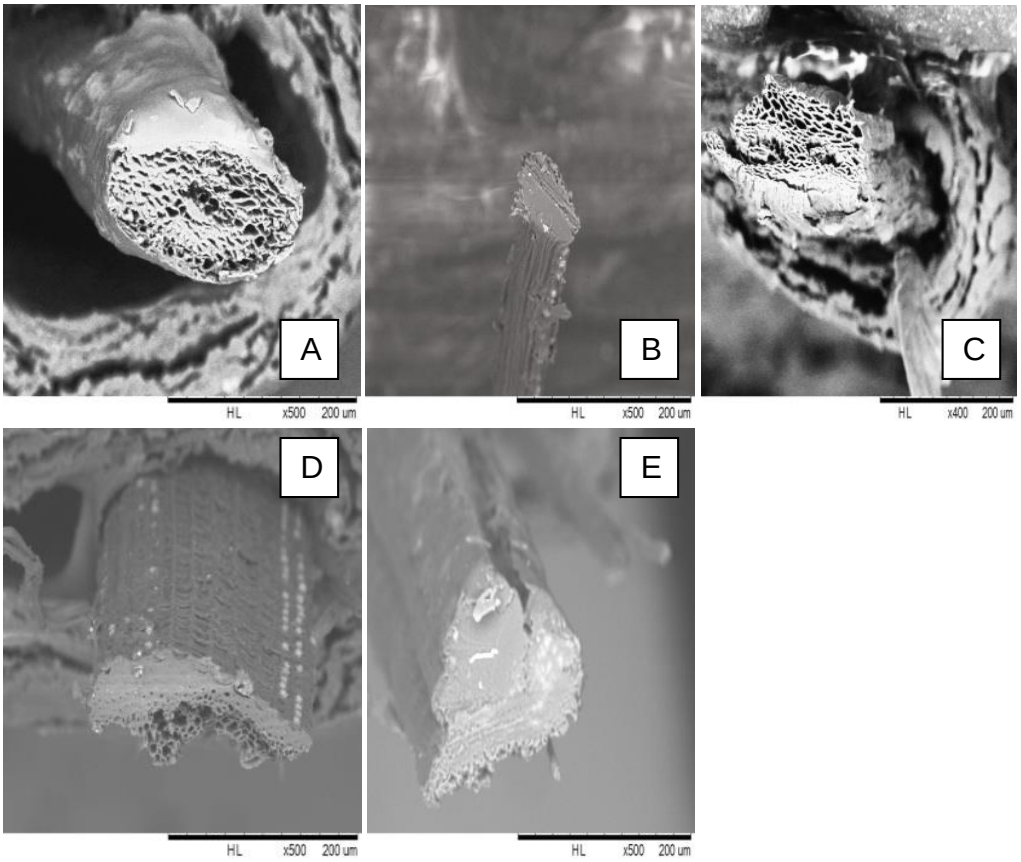

Fig. Y. SEM of technical fibers (raw fibers) of spath (A), sheath (B), bunch (C), leaflet 1 (D) and leaflet 2 (E) are given below. (bar = 200 µm)