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In-depth study of agave fiber structure using Fourier transform infrared spectroscopy

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ABSTRACT

FTIR spectroscopy is a powerful method to analyse materials and especially fiber structure. This technique is largely used to obtain quick information on the fiber composition and to detect possible transformations after physical and chemical treatments. Unlike other techniques, FTIR is a quick method which demands a reduced amount of fibers. Furthermore, it is a non destructive method especially for Attenuated Total Reflectance (ATR), and Near Infrared (NIR) spectroscopy which are nowadays widely used.

In this work, FTIR spectrum of agave fiber has been thoroughly investigated. Because of its complexity, the spectrum was separated into two regions: CH and hydrogen bond stretching (>2500 cm^{-1}) and "fingerprint" region (<2000 cm^{-1}). A detailed study of intermolecular and intramolecular chains was made.

Infrared ratios (Lateral Order Index, Total Crystallinity Index, and Hydrogen Bond Intensity) were used to study the crystallinity and the degree of regularity of agave fiber.

1. Introduction

During the last few decades, natural fibers reach the interest of many research works all over the world due to their attractive properties. Besides renewability and biodegradability, fibers are characterized by their good availability, low cost and density, limited damage to the processing equipment, and reasonable strength and stiffness.

In Tunisia, many local natural fibers have been studied in order to evaluate their textile potential and to use them in development of new textile and paratextile products. Particularly, agave Americana L. fiber, which originates from Central America and grows abundantly in North Africa, constituted the subjects of many studies (El Oudiani, Chaabouni, Msahli, & Sakli, 2009; Msahli, 2002; Msahli, El Oudiani, Sakli, & Drean, 2015). To evaluate textile potential of this local vegetable fiber, a methodology composed of many steps was adopted: extraction and separation of technical and elementary fibers, characterization of the main textile properties, intrinsic variability study, fine structure characterization, surface modification...

The main results show that agave fiber excels other natural fibers in some mechanical and physical properties such as stiffness, rigidity, extensibility, density... (Msahli, 2002; Msahli et al., 2015) and thus agave fiber provides many advantages when used as reinforcement of composite materials (El Oudiani et al., 2009).

However, a large part of work conducted to characterize the structure of agave fiber, was only based on SEM and Xray diffraction methods (El Oudiani, Chaabouni, Msahli, & Sakli, 2011; El Oudiani, Chaabouni, Msahli, & Sakli, 2012a, 2012b; El Oudiani, Ben Sghaier, Chaabouni, Msahli, & Sakli, 2012c). To date, no work has been performed on the structure analysis of agave fiber by the use of Fourier transfrom infrared spectroscopy. In fact, this technique seems to be one of the most interesting methods used by many researchers to evaluate accurately the composition of lignocellulosic materials in terms of wood, cellulose and lignin structure. (Akerholm, Hinterstoisser, & Salmen, 2004; Cael, Gardner, Koenig, & Blackwell, 1975; Fengel and Ludwig, 1991; Hinterstoisser & Salmean, 2000; Ilharco & Barros, 2000; Kokot, Czarnik-matusewicz, & Ozaki, 2002; Liang & Marchessault, 1959a, 1959b; Michell, 1990; Proniewicz et al., 2001; Schwanninger, Rodrigues, Pereira, & Hinterstoisser, 2004; Siesler, Krâssig, Grass, Kratzl, & Derkosch, 1975; Sugiyama, Persson, & Chanzy, 1991; Watanbe, Morita, & Ozaki, 2006).

The observed spectroscopic signals are due to the absorption of infrared radiation that is specific to functional groups of the molecule. The absorption frequencies are related to the vibrational motions of the nuclei of a functional group and present height and position modifications when subjected to chemical treatments (Hori & Sugiyama, 2003; Pandey, 1999).

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In this work, a thorough analysis of agave fiber infrared spectrum was conducted to further investigate the structure of this fiber and subsequently the chemical and structural changes which can take place in the fiber components after different treatments (natural or artificial aging oxidation, thermal degradation, etc.).

2. Experimental methods

2.1. Sampling

The leaves of agave americana L. involve a composite structure composed of an organic matrix reinforced by cellulosic microfibers. This structure shows many kinds of chemical bonding such as covalent, hydrogen or Van Der Waals bonds. The organic matrix includes several components like hemicelluloses, pectic matter, lignin and gums; whereas the reinforcing fibers are mainly composed of cellulose.

To extract fibers from the organic matrix, different methods can be used (mechanical extraction, chemical extraction, biological extraction...). These methods have a great influence on the fine structure of the obtained fibers (Chaâbouni, 2005; El Oudiani et al., 2009; Msahli, 2002; Msahli et al., 2015). In this work, we have used the distilled water extraction method which seems to yield acceptable mechanical properties. In this method, leaves are submitted to a hydrolysis treatment in distilled water. Subsequently, fibres are separated from the matrix by calendering the leaf and then washed. A temperature of 120 °C and duration of 90 min appear to be the best conditions for the treatment as demonstrated in a previous study (Chaâbouni, 2005).

As a result of the extraction, we obtain technical fibers presented as fibrous bundles called bundles of elementary fibers. Mechanical and physical characterisation of the obtained fibers was made (El Oudiani et al., 2009). The main results show that agave fiber has a tenacity at the order of 30.2 cN/tex, an elongation of 33%, a density of 1.15, a fineness at the order of 21.2 tex and a degree of crystallinity of 50.1%. The cellulose content is 65.2% and the lignin content is 2.7%.

2.2. Spectroscopic characterization

Transmittance FTIR spectrum was measured using the KBr pellet technique. An amount of 2 mg of dried agave fibers was milled and dispersed with 100 mg of potassium bromide KBr. Then the mixture was pressed to obtain tablets with a thickness of 1 mm (pressure of 8 bar). The studied spectrum represents average of ten.

Spectrophotometer of type Nicolet 510 M with a resolution of 2 cm^{-1} and 100 scans were taken per sample. The infrared spectra were recorded in the range of 4000–500 cm^{-1}.

The analysis of agave fibers structure was established by the examination of 4 different regions of 1-D IR spectrum.

Processing of spectra, baseline corrections, derivative spectra and band deconvolution methods was generated using software resolution program (Origin 6.0). We have used Gauss function to fit peak profiles. By choosing the appropriate parameters of this function, we obtain a minimum difference between theoretical and experimental profiles.

3. Results and discussion

Fig. 1 shows the typical Infrared spectrum recorded for agave fiber. At first sight, we can divide this spectrum into two different zones. The zone at the right side (superior to 2000 cm^{-1}) which comprises fewer peaks, even though we can find some discrete information from this zone. In fact, CH alkane stretching at about 2900 cm^{-1} proves the presence of saturated carbons,

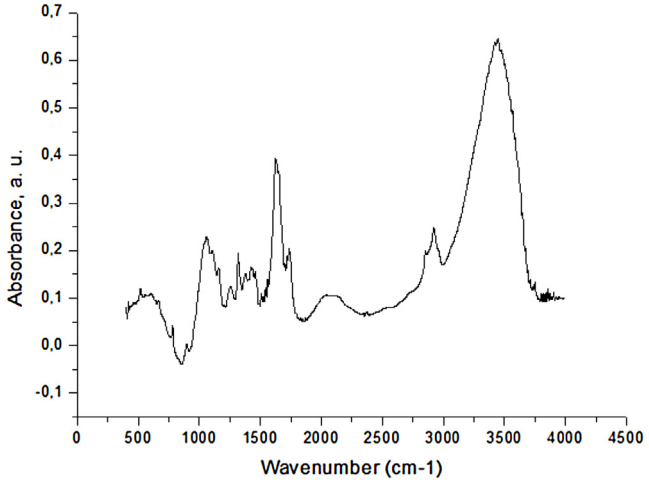

Fig. 1. IR spectrum of agave Americana L. fiber.

whereas, bands above 3000 cm^{-1} indicates the presence of unsaturated carbons. In fact, the large band between 3200 and 3700 cm^{-1} is attributed to the hydrogen bonds.

However, the zone at the left side of the spectrum (inferior to 2000 cm^{-1}), includes significantly more peaks with different absorption intensities. The absorption of double bond groups (carbonyl) is well identified by the presence of a strong peak around 1600 cm^{-1}. The single bond C-O is identified by absorptions at 1100–1300 cm^{-1}. This complicated zone with multiple absorption peaks inferior to 2000 cm^{-1} is called "fingerprint region".

To give more precise information, we have further subdivided IR spectrum of agave fiber into four regions: one region for hydrogen bond (3800–2800 cm^{-1}) and three for the fingerprint region (1800–1550 cm^{-1}, 1550–1200 cm^{-1} and 1200–850 cm^{-1}). The region 1800–2800 cm^{-1} was not studied since there is no presence of alkyne or nitrile groups in the fiber structure.

Besides, to more understand the IR spectrum, and to determine the total absorption and the position of all bands, we have deconvoluted the four studied regions.

3.1. OH bond region

A hydrogen bond may be defined as an electrostatic attraction occurring between polar groups and involving on one side a hydrogen atom and on the other side a highly electronegative atom like nitrogen, oxygen or fluorine. Within the material structure, hydrogen bond can arise between adjacent molecules (case of intermolecular OH bond) or between different parts of a same molecule (case of intramolecular OH bond). The hydrogen bond energy depends on molecular conformation and climate levels (temperature and humidity conditions). It ranges from 5 KJ/mole for weak bonds to 30 KJ/mole for strong bonds. Thus, hydrogen bond is stronger than van der Walls interactions, but weaker than covalent and ionic bonds (IUPAC, 2006).

In cellulosic structure, hydrogen bonds may be found in both crystal and amorphous regions. Many researchers have attempted to find relationship between cellulosic structure and hydrogen bonds. Since 1913, Nishikawa and Ono studied the crystalline structure of cellulose using X-ray diffraction method (Salmén & Åkerholm, 2005). They conclude that cellulose has four polymorphic structures (cellulose I, cellulose II, cellulose III and cellulose IV). The two first polymorphs (cellulose I and II) were largely studied, unlike cellulose III and IV which are still under examination and must be more considered.