STUDIES OF THE COMPOSITE APERIODIC NANOSTRUCTURE OF NATURAL VEGETABLE FIBERS

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Introduction

Vegetable fiber is a wonder of the nature, the most important and widespread natural organic polymer. In order to take full advantage of this considerable and precious raw material source, one needs basic studies in order to find effective treatment and modification methods. For instance, in order to manufacture cotton faster and jute or pineapple fibers softer. These aims can only be attained when the inside structure of the fiber and its relationship to specific fiber features are sufficiently known.

The chemical structure of the native cellulose, one of the basic components of the natural vegetable fiber, as a linear β-1,4 - Glucose chain is well accepted. However, the physical structure that creates the wonderful fibred network of the supermolecular order of the vegetable fiber is not yet completely clear.

From our experiments over a long period of time on different genera of vegetable fibers (such as cotton, jute, pineapple, sisal, bamboo), we have discovered that the inside structure of the vegetable fiber is constituted not only by polysaccharide cellulose, but also by another very important component consisting of the Fivefold [2Fe-2S] Spin super-exchange OrganoMetallic combinations. These persist in the form of the Composite Aperiodic Crystal Nanostructures diagonally linking the cellulose chains and creating an internal stereoconformational architecture and wonderful features of vegetable fibers (such as the strength, the torsional module, the conductivity, the radiation response). We have also investigated some physical and biological treatment engineerings to improve the properties of the real vegetable fibers.

Experimental

A combination of experimental methods have been used :

1) Chemical treatment for removing the leaf glues; 2) Measurements of mechanical & physical parameters of the fibers: the sizes, the torsion modulus, the tensility, the critical stress for rupture, etc; 3) X-ray diffraction involves those regions so ordered as crystalline; 4) SEM-recording to observe the surface of the "practical fiber"; 5) ESR studies involve Spin Complexes and related molecular-electronic structures and dynamics in the fiber network; 6) Light polarization for visibly confirming the crystalline domains as well as the effective symmetry of the "practical fiber"; 7) Special physical and biological treatments for improving fiber properties.

The ESR studies play here a decisive role in the revelation of the [2Fe-2S] fivefold complexes composite in the network as well as of the nanostructure of the fiber. The ESR studied patterns have been obtained from the different bundles of parallelized fibers (Fig. 1a) and the different samples of crumbs of fibers (Fig. 1b). The pattern temperature was controlled at the different values from -196°C to +150°C.

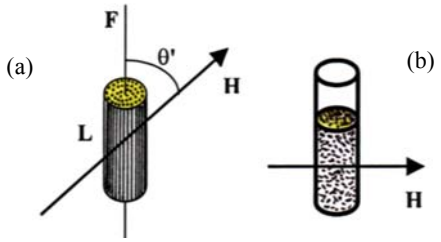

Fig. 1 ESR pattern of fibers: (a) A bundle of parallelized pratical fibers of the length L and (b) A sample of crumbs of fibers contained in a quartz ampule. H is the applied magnetic field.

Some Results and Discussion

OrganoMetallic combination [2Fe-2S] in the fibers

In the natural vegetable fibers persists a very strong spin super-exchange combination [2Fe-2S] from two Iron atoms and two Sulfur atoms (fig. 2). In this rhombic combination exists a permanent electron spin coupled pair [Fe-Fe] of the low spin ions Fe^{3+} with a spin number of 10^{19} – 10^{20} spin/gram. There is also a hyperfine structure interaction of the Fe^{3+} electron spin with the nuclear spin of ^{33}S (I = 3/2 at the natural abundance of 0.76%).

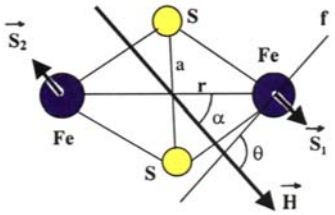

Fig. 2 Spin super-exchange coupled combination [2Fe-2S]: **r** is the length of the coupled pair [Fe-Fe]. **f** is the principal axis of the local crystal field acting on the spin center Fe. This axis is just the local axis of the called elementary fibril (Nanofibril) **f** which creates the local crystal field. **H** is the applied magnetic field, **$\alpha \equiv$ (r,H)** and **$\theta \equiv$ (f,H)**.

For invesgating the inside stereoconformational structure of the vegetable fiber, it is especially applied and developed here a new method, called ESR structural tomography (ESR-ST): We compute the non-visible inside structural parameters of the fiber by using a sufficient set of ESR data from the whole ensemble of the super-exchange combinations [2Fe-2S] as the "intelligence centers", lawfully distributed in the fiber. These

data are measured at the different θ'-directions of the applied magnetic field H (Fig. 1). The angle θ' is a directly observable parameter.

The helix structure of vegetable fibers

This concrete helix structure has been discovered by the measurements of the θ'-angular dependence of the g-factor. A called macroscopic "practical fiber" F (Fig. 3) consists of a lot of "elementary fibrils" (Nanofibrils) spiraling together about its axis by a sloping angle $\theta_0 = 54.7°$. This phenomenon can be surficially observed by the SEM-recording (Fig. 4).

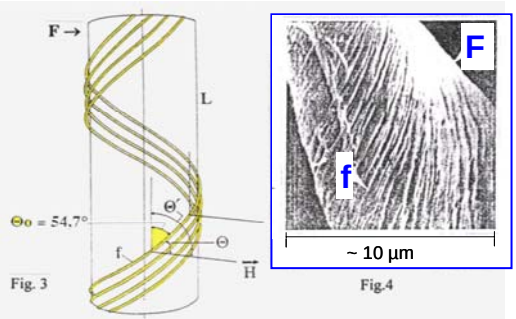

Fig. 3 Fig.4

Fig. 3 Simplified model of the physical structure of a practical fiber F. In ESR measurements, only θ'≡(F,H) can be directly observed. **Fig. 4** A SEM-recording (~x 3000) of a practical fiber.

The revealed characteristical value of the spiral angle θ_0 is of a deep significance on the quantum dynamics of the active electron system in the fiber as well as on the statistically macroscopic properties of the fiber.. This peculiarity also can be confirmed by the light polarization experiment on the fiber.

The [2Fe-2S] fivefold metallo-organiccomplex structure composite in vegetable fibers

The measurements of the angular dependence of the ESR spectra from the rhombic combination [2Fe-2S] showed that the symmetry axis of the respective local crystal field is not the F axis of the practical fiber but the f axis of the elementary fibril (Nanofibril). Therefore evidently, the disposition of each rhombic combunation [2Fe-2S] to this f axis will be a decisive factor to compose the stereoconformational structure of the [2Fe-2S] multifold complex in the elementary fibril.

The calculations on the basis of the measured data give the values of the length r and the tilt angle δ_0 of the coupled pair [Fe-Fe] and the length a of the coupled pair [S-S] (Fig. 5):

$$\delta_0 = 39.3^0\ ,\ \ r(Fe\text{-}Fe) = 3.395\ Å,\ \ a(S\text{-}S) = 1.560\ Å$$

The result of r corresponds with the well known distance of 3.39 Å between the Fe atoms non bonding with each other. The result of a entirely corresponds with the well known length of 1.56 Å of the sulfur haltere pair in the mineral pyrite, a natural compound inherited from vegetation.

With the disposition parameter set (δ_0, r, a) corresponding to each rhombic combination [2Fe-2S], the pavage angle unit β in the plane perpendicular to the f axis (Fig. 5) is

$$\beta = 2\mathrm{arctg}\frac{a}{r\sin\delta_o} = \frac{2\pi}{5}.$$

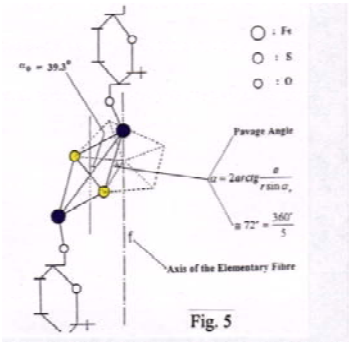

Fig. 5

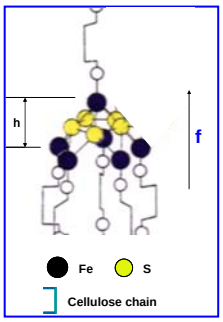

Fig. 6

Fig. 5 A [2Fe-2S] super-exchange coupled combination diagonally linking two cellulose chains. This disposition corresponds with the pavage angle unit $\beta = 2\pi / 5$ in the plane perpendicular to the f axis.
Fig. 6 The basic unit of the [2Fe-2S] Fivefold OrganoMetallic Aperiodic Nanostructure of vegetable fibers.

These experimental events enable to revealing the **basic unit** of the Fivefold OrganoMetallic Aperiodic Nanostructure composite in the fibred network as illustrated in Fig. 6. Every this basic unit showes a pyramid coupled by five [2Fe-2S] rhombic combinations diagonally linking one cellulose chain (above) with five following ones (below). The pyramid is based on a pentagon created by five sulfur atoms, whose plane is perpendicular to the f axis of the elementary fibril. On the energy aspect, this fivefold spin exchange coupling can bring out a maximal convenience.

The **elementary cell** of the OrganoMetallic structure coupled by the 12 adjoined fivefold [2Fe-2S] basic units diagonally links the 9 cellulose chains (above) with the 9 ones (below) and creates **an elementary fibril as a Nano Wire** as illustrated in Fig. 7.

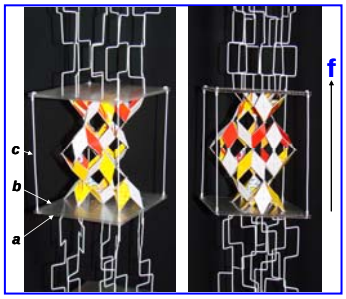

Fig. 7 Monoclinic Elementary Cell:
γ = (b,a) = 72°, c // f , a = b = 8.180 Å, c = 10.509 Å

Conclusion

From the experimental results of ESR in combination with other methods, especially with the developed "ESR Structural Tomography", on different genera of natural vegetable fibers, their very original Composite 54.7°-Helix Fivefold [2Fe-2S] OrganoMetallic Aperiodic Nanostructure, with its very unique Basic Units as well as Elementary Cells, has been revealed and interpreted. This Composite OrganoMetallic Nonostructure plays a decisive role in the very peculiar and useful features of the vegetable fibers. On this basis, one can elaborate essential and efficient biophysical engineerings to improve the applied properties of natural vegetable fibers.

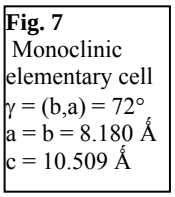

Fig. 7
Monoclinic elementary cell
γ = (b,a) = 72°
a = b = 8.180 Á
c = 10.509 Á