Moroccan Cedar softwood study: Application of FT-Raman spectroscopy

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Abstract. As non-destructive technique, FT-Raman spectroscopy has been used to study the molecular structure and monitor changes in the composition of carbohydrates and lignin components containing wood materials. For this purpose, four samples originated from Moroccan cedar wood were analyzed. Following the FT-Raman spectra, it was found that carbohydrates were identified by the bands at 898, 1098, 1123 and 1456 cm^{-1}, while lignin matrix was evaluated by the bands at 1657, 1598 and 1267 cm^{-1}. The decrease of the intensities related to these feature bands reflects the effects of natural degradation phenomenon and shows the evidence of chemical changes and quick deterioration of these contents upon exposure time to natural degradation process. Thus, the FT-Raman tool has the potential to be one of crucial sources to characterize composite materials and to evaluate the chemical changes occurred on their structures under the influence of physico-chemical or biological attacks without causing any damage of the wood surfaces or their supports.

1 Introduction

Moroccan softwood, as one of the most abundant materials on earth, is provides a resource of great value for construction and production of novel objects since antiquity. It is extensively used for many applications (artworks, packaging industry, shipbuilding, furniture, paper pulp, eating utensils, etc) since antiquity.

These materials have a heterogeneous and complex structure, primarily consisting of cellulose, lignin and hemicelluloses components which are reported as one group of materials with a well-known reputation for susceptibility to natural deterioration. The exposition to combined conditions of physical, chemical and microbial attack as ultraviolet (UV) light, solar irradiation, moisture (humidity), temperature and fungus can cause molecular degradation of their main components. It results a loss of fiber strength and rigidity. This is manifested in lower mechanical stability that may leads, sometimes, to full disintegration of wooden materials [1], and consequently results in loss of cultural heritage [2].

Hence, an accurate characterization and examination of different changes occurred in these materials through a spectroscopic study by non-destructive techniques, is extremely important for optimal safeguarding and preservation.

A very few works have been conducted on structural characterization and/or structural degradation of wood by Fourier transform Raman spectroscopy (FT-Raman) [3-6], in contrast to the other spectroscopic techniques which are the most used for material's study as Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and nuclear magnetic resonance (NMR). In this field, Agarwal and Ralph [3] have applied FT-Raman technique to identify the major constituents of black spruce wood: lignin, cellulose and hemicelluloses, while Ona et al. [7] have performed interesting researches on the Eucalyptus wood properties by the same technique.

Recently, FT-Raman is being more performed for the chemical analysis of biomaterials as wood [8-9]. It provides more information about polymer chain and fundamental knowledge at a molecular (micro-level) and macro-level [10]. In addition, it has been shown to be a valuable technique for analyzing structural changes in the fibers which arise from physical, chemical or mechanical processing [11-12]. Hence it is possible to perform fast, non destructive and non invasive measurements without extensive sample preparation [9].

As this non-destructive spectroscopic method seems to be a promising instrument for studying composition of wood materials, the main goal of the present work is to investigate, in details, the distribution of chemical composition in softwood materials and understand the structural rearrangement caused by the effect of natural degradation process.

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1 Materials and methods

1.1 Sampling

Analyzed Softwood samples were collected from four archaeological Cedar wood (*Cedrus atlantica*) dating to the 18th, 19th, 20th and 21st centuries in the Ecomuseum of Tazekka under standard climate. The pieces originate from Tazekka national park (WGS84: 34°6′0″N, 4°11′0″W) located in the Middle Atlas of Morocco and near the city of Taza (Bab Boudir region). The samples were dated by specialist researchers using Radiocarbon dating method. Thus, the dimensions of wood samples are 200×200×100 mm^3 (tangential × radial × longitudinal directions). The characteristics of the experimental materials are presented in Table 1. The FT-Raman analysis was performed directly on the surface of the samples.

Table 1. Sample's description.

Sample	**Age (**century)
D_1	21^{th}
D_2	20^{th}
D_3	19^{th}
D_4	18^{th}

1.2 FT-Raman spectroscopy

The FT-Raman study was conducted with a Bruker (USA) MultiRAM Stand Alone FT-Raman Spectrometer. The instrument is equipped with a diode-pumped Nd:YAG excitation source with a large emission intensity at 1.064 nm. Furthermore, the signal was collected with a liquid nitrogen cooled germanium detector. For each FT-Raman measurement 100 scans were averaged, with a resolution of 4 cm^{-1} and a time measurement of 3 min for each spectrum. All FT-Raman spectra were registered from 4000 to 250 cm^{-1}. Three analyses were performed on several locations for each sample. The temperature and humidity room were controlled during analysis.

3 Experimental results

The common bands assignments of four wood's sample (D_1, D_2, D_3 and D_4), are given in Table 2. The band's attribution was extremely difficult due to the overlapping of some cellulose and lignin bands; and so, it confirmation was based on different literature data [5, 6, 13] which focused on the wood study and investigation of degradation effect using FT-Raman spectroscopy.

Table 2. Assignment of characteristic FT-Raman bands of softwood materials (D_1, D_2, D_3 and D_4) [13-21].

Wavenumber (cm^{-1})	Assignment
2943	□ CH (asymmetric) in OCH_3 of lignin
2895	CH_2 group in the glucopyranose ring of cellulose I_β
1657	Conjugated C=C stretching of coniferyl alcohol (guaiacyl) in lignin that overlaps with C=O stretch of coniferyl aldehyde
1598	□ C=C aromatic skeletal vibration typical for lignin guaiacyl and syringyl monomer in lignin
1456	HCH bending and small proportion of HOC bending in pure or amorphous cellulose
1378	δ(C-H) and δ(CH_2) in cellulose and hemicelluloses
1333	C-H vibration in cellulose and C-O vibration in syringyl derivatives
1267	C_{ar}-O of aryl-O-CH_3 and/or aryl-OH of guaiacyl/syringyl monomer aromatic ring
1123	Stretching vibration of C-O, C-O-C glycosidic linkage in cellulose and xylan or C-C ring
1092	
898	CH deformation in amorphous cellulose
379	δ_s(CCC) in crystalline cellulose

Figure 1 reports the representative FT-Raman spectra for each sample (D_1, D_2, D_3 and D_4) between the spectral region of 3500-500 cm^{-1}.

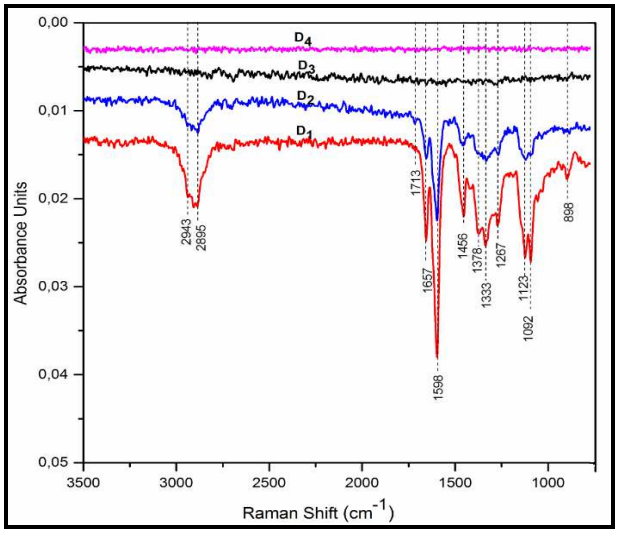

Figure 1. FT-Raman spectra acquired from the four samples of softwood: D_1- Wood sample dating to 21^{st} century; D_2- Wood sample dating to 20^{th} century; D_3- Wood sample dating to 19^{th} century; D_4- Wood sample dating to 18^{th} century.

3.1 Cellulose and hemicelluloses

The main characteristic FT-Raman signals for cellulosic and hemicellulosic fibers can be visually divided into

two essential regions: 3500-2800 cm^{-1} and 1480-250 cm^{-1} fingerprint region (Fig. 1 and 2).

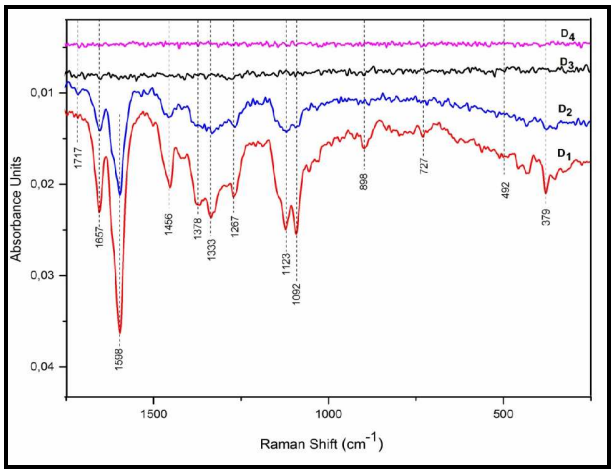

Figure 2. FT-Raman spectra 1750-250 cm^{-1} range acquired from the four samples of softwood: D_1- Wood sample dating to 21st century; D_2- Wood sample dating to 20th century; D_3- Wood sample dating to 19th century; D_4- Wood sample dating to 18th century.

For the first region, the detected bands are mainly due to the hydroxyl groups, methyl and methylene stretching vibrations. Concerning the second range, the bands correspond to methylene, methyl bending, wagging, rocking, C-O-H in-plane bending and C-O-H in-plane bending and skeletal bending vibrations (CCC, COC, OCC and OCO). Thus, the deterioration of the cellulose and hemicelluloses fractions has been explained by the decline in intensities of these bands (Fig. 1) during exposure to natural atmospheric effect.

The recent samples dating to 21st and 20th century (Fig. 1. D_1 and D_2) clearly display a feature band at 2895 cm^{-1}. According to Barnette et al. [13], the latter was attributed to symmetric stretching vibrations of the CH_2 group in the glucopyranose ring of cellulose I_β. The presence of this band in spectra of D_3 and D_4 (Fig. 2) degraded samples dating to 19th and 18th century respectively, suggests that upon a long exposure to the degradation phenomenon, the crystalline fraction decomposes and results disorder fraction which in turn re-crystallized and formed the new ordered fraction. This finding can be confirmed by the decline in intensities of feature bands typical of amorphous cellulose at 1456 cm^{-1} and 898 cm^{-1} and assigned to HCH bending and small proportion of HOC bending in amorphous cellulose as well as CH deformation in amorphous cellulose, respectively [14]. On the other hand, the C-H and CH_2 deformations in cellulose and hemicelluloses compounds were observed at 1378 cm^{-1}.

From spectra of sample D_1 and D_2 (1200-1000 cm^{-1}), it is easily to distinguish a doublet of peaks at 1123 and 1092 cm^{-1} assigned to combined stretching vibration of C-O ring and C-O-C glycosidic linkages in cellulose and hemicellulose [13, 15]; providing information about the breaking of cellulosic chains at the β-1,4-glycosidic ether bonds. Thus, the disappearance of these two bands in spectra of oldest samples (Fig. 2 D_3 and D_4) indicates the serious degradation occurred on cellulose and hemicelluloses.

Referring to literature data [16], the bands at 379 cm^{-1} can be unambiguously attributed to CCC deformations in crystalline fraction of cellulose. Fig. 2 shows a discernible decrease of this band proportionally with the age of sample, indicating the loss in mechanical rigidity and toughness for these materials, consequently, the surrender of lignocellulosic biomass against deconstructive processes.

The weak features at 379 and 440 cm^{-1} might be explained as a result of intermolecular interactions between lignin and carbohydrates, that can caused a small shifts in peak positions and/or changes in band shapes [3].

3.2 Lignin

In order to estimate lignin fraction, different bands were studied. In the region between 3100-2800 cm^{-1}, the band at 2943 cm^{-1} was attributed to the C-H stretching of the methoxy groups in lignin [5, 6]. It appears less pronounced in the oldest samples dating to the 19th and 18th centuries (Fig. 1 D_3 and D_4) indicating lower lignin presence compared to the youngest ones (Fig. 1 D_1 and D_2).

The detection of feature band at 1717 cm^{-1} in spectra of samples D_2, D_3 and D_4 (Fig. 2) indicates the presence of carbonyl groups related to the residual lignin amount resulted from delignification of wood sample upon process of natural degradation. It relative intensity appears no changeable for all oldest samples, while it appears absent in D_1 spectrum (Fig. 2). The non important sensitivity of this produced amount to degradation events is the possible explanation in this case.

Furthermore, the combined band in the region between 1657 and 1598 cm^{-1} was mainly originates from guaiacyl (coniferyl alcohol units for softwood) and syringyl (sinapyl alcohols units for hardwood) matrix in lignin compound. The band detected at 1657 cm^{-1} is attributed to conjugated C=C stretching vibration of coniferyl alcohol (guaiacyl) in lignin that overlaps with C=O stretch of coniferyl acid after oxidation of alcohol in side chain [6, 17]. According to Kihara et al. [18], this band can also assigned to marker bands for conjugate carbonyl groups (α,β-unsaturated C=O).

The most intense peak at 1598 cm^{-1} (Fig. 2 D_1 and D_2) is attributed to stretching vibration of polar aromatic C=C in phenolic compounds [19] related to guaiacyl and syringyl monomers in lignin [5, 20].

The other predominant lignin band was detected at 1267 cm^{-1} and corresponds to $C_{aromatic}$-O of guaiacyl lignin for softwood [17]. It shifted to lower intensities during exposure time to natural degradation process (Fig. 2), because of guaiacyl lignin is less susceptible than syringyl lignin. Nevertheless, for hardwood spectra, there is a rapid decline in its intensity. Thus, we can confirm that our cedar samples belong to the softwood specie.

It is likely reported that decomposition of hemicelluloses and/or extractives, can lead to the decrease in quantity of lignin, consequently, a simultaneous deterioration of wooden materials.

4 Conclusions

The present work has put in evidence the crucial role of FT-Raman spectroscopy as non destructive method to characterize and study the effect of natural degradation on chemical structure of cellulose, hemicelluloses and lignin as major components of softwood by providing accurate information about their chemical structures. Based on the obtained results, the gradual decline in intensities of features bands related to these constituents for each compound of wood, suggest their sensitivity to combined degradation agents and, consequently, irreversible losses of softwood material in archaeological sites.

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