FTIR SPECTRAL DATA OF WOOD USED IN ROMANIAN TRADITIONAL VILLAGE CONSTRUCTIONS

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abstract: Oak, fir, acacia and hornbeam wood samples, used in the construction of farm buildings from Arges county, were studied by FTIR spectroscopy to emphasise effects of natural conditions on wood aging. The analyzed wood was indoor and outdoor exposed for different periods between 40 to 100 years. FTIR spectra of the different aged tree species show the characteristic bands of lignin and carbohydrates, only small shifts in position and intensity being observed. The lignin content was determined from the C=C band intensity. The lignin content decreased with the usage period, this finding being confirmed by the relative change in the ratio lignin/carbohydrate reference bands for the oak samples.

Introduction

Wood artefacts with patrimonial value are very often degraded due to bacterial attack. Traditional procedures of conservation uses toxic agents and their use should be limited. Gamma irradiation of wood artefacts proved to be an efficient procedure but there are only few scientific studies on this subject. Our goal is to characterize with spectroscopic methods the physical chemical changes induced in wood by gamma irradiation. Samples of wood profiles, traditionally used in the construction of farm buildings could be a good model for naturally aged wood. Changes in FTIR bands intensity and position could be a good indication on the chemical and structural changes of decayed wood.

Recent literature contains studies on wood degradation induced by bacterial attack, UV-visible light irradiation or accelerated weathering [1-3]. Also, the effect of photo-irradiation on the surface chemistry of wood, the influence of extractives on the photo discoloration, the surface analytical characterization of water repellent acylated and silylated wood samples, the influence of viscoelastic thermal compression on the chemistry and surface energetics of wood, the influence of xylem growth ring width and wood density on durability of oak heartwood and the behaviour of nanoparticle (ultrafine) titanium dioxide pigments and stabilisers on the photooxidative stability of water based and isocyanate based

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acrylic coatings were investigated [4-9]. In all the named cases were used specific measurements and the highly selective FTIR spectroscopy method.

For a better understanding of the bacterial wood-degradation process, some investigations were performed looking at chemical changes of wood during degradation and at living conditions and environmental factors affecting degradation [1]. Bacterial degradation results in a reduction of hollocellulose content therefore in an increase of relative amount of lignin. In softwood samples it was observed that the lignin content decreased from outside to inside. In the oak samples the average lignin content of degraded wood was 44.6% compared with 25.9% obtained from sound oak. The chemical analysis results were confirmed by FTIR spectrometry. The largest peak form 1020 cm^{-1} is assigned to bonds of hollocellulose. The peaks at 1217 cm^{-1}, 1265 cm^{-1}, and 1505 cm^{-1} are assigned to lignin and corresponds to CO bending vibrations of guaiacyl ring and C=C stretching vibrations in aromatic rings [1].

The main factor responsible for wood photodegradation is lignin, which absorbs UV/Vis light because of its chromophoric groups. The degradation mechanism is complex with different paths leading to water soluble products and finally to chromophoric groups like carboxylic acids, quinines or hydroperoxides [2].

The weathering process is initiated by sunlight and its rate is enhanced by moisture (humidity), temperature, air and the pollutants which are abundantly present in the outdoor environment. Apart from number of environmental parameters that contribute significantly to the degradation of wood the rate of degradation may also be affected by the wood properties, *e.g.* presence of extractives and kind of wood. The chemical composition of constituent polymers of wood is different. For example, hardwood lignin, termed guaiacyl-syringyl lignin consist of coniferyl alcohol and sinapyl alcohol derived units in varying ratios, whereas in softwood lignin, usually refered to as guaiacyl lignin, the structural elements are derived principally from coniferyl alcohol (more than 95% of the total number of structural units) with the remainder consisting of mainly *p*-coumaryl alcohol type units [4]. It is known that hardwoods degrade at a slow rate than softwoods [3].

In this work outdoor and indoor exposed samples of hardwood (oak, acacia, hornbeam) and softwood (fir) were studied by transmittance FTIR spectroscopy to emphasize chemical and structural effects of natural aging conditions [10].

Experimental

With the help of a razor few milligrams of probe were obtained form the center of freshly cut wood pieces presented in the Fig. 1.

The KBr technique was used for sample preparation. Spectra were measured at a resolution of 4 cm^{-1} and 16 scans were recorded per sample. Bruker Vertex 70 FTIR spectrometer and the OPUS software were used. Spectra in the range 4000–400 cm^{-1} were baseline corrected and atmospheric compensation was done.
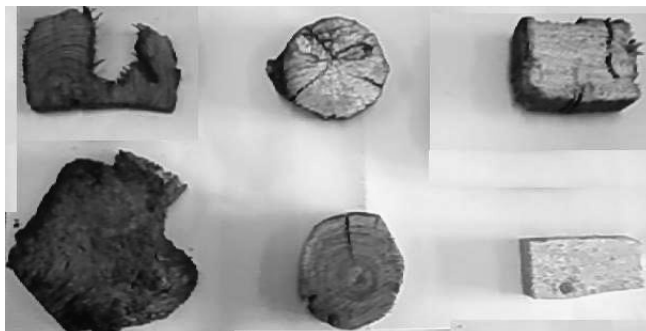
Fig. 1 Wood samples, from left to right: top acacia 50 years from farm cottage, 40 years hornbeam, 70 years fir used as house roof pillar, bottom 100 years oak from granary, 40 years oak, new fir

Results and discussion

The obtained FTIR spectra, given in the Fig. 2 show the same basic structure: a strong broad O-H stretching at 3300–3600 cm^{-1}, C-H stretching at 2800–3000 cm^{-1} and several distinct peaks in the fingerprint region between 500 and 1750 cm^{-1}. Most of these bands have contributions from both carbohydrates (cellulose and hemicellulose) and lignin.

In order to determine the rate of lignin decay and carbonyl formation, the intensities of the carbonyl absorption band at 1734 cm^{-1}, lignin reference band at 1506 cm^{-1} and carbohydrate reference bands at 1374 and 1158 cm^{-1} were measured and their ratios were calculated (see Table 1). Heights of peaks were measured from the baseline constructed by connecting the lowest data points on either side of the peak. A vertical line is then drawn from top of the peak to the X-axis. The portion of the line between the top of the peak and the baseline represents the corrected peak height [4].

As can be seen from the Table 1, for the oak samples the ratios lignin/carbohydrate and carbonyl/carbohydrate decrease with the period of wood exposure. The other samples do not follow a trend. For further analysis the milling of samples must be done to obtain homogenous mixtures. More spectra should be acquired and their media should be used.

Preliminary results of IR spectra analysis of 10 lignocelluloses indicate that the following non-linear equation describes well the relation between the Klason lignin[a] content and the height of the 1505 cm^{-1} band:

$$\% \text{ lignin} = -1.23 + 193.4\,x - 279.8\,x^2$$

where x = band intensity determined by the baseline method (validity for lignin contents between 30-5%) [11].

Using the above equation the following lignin content was determined: fir, 70 years 14.90% fir, new 19.30%, oak, 40 years 18.07%, oak, 100 years 10.47%, acacia, 50 years 12.15%, hornbeam, 40 years 18.07%.

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[a] Klason lignin names the unhydrolyzed residue obtained in the standardized hydrolysis procedure of the wood polyssacharides with 72% sulphuric acid [11].
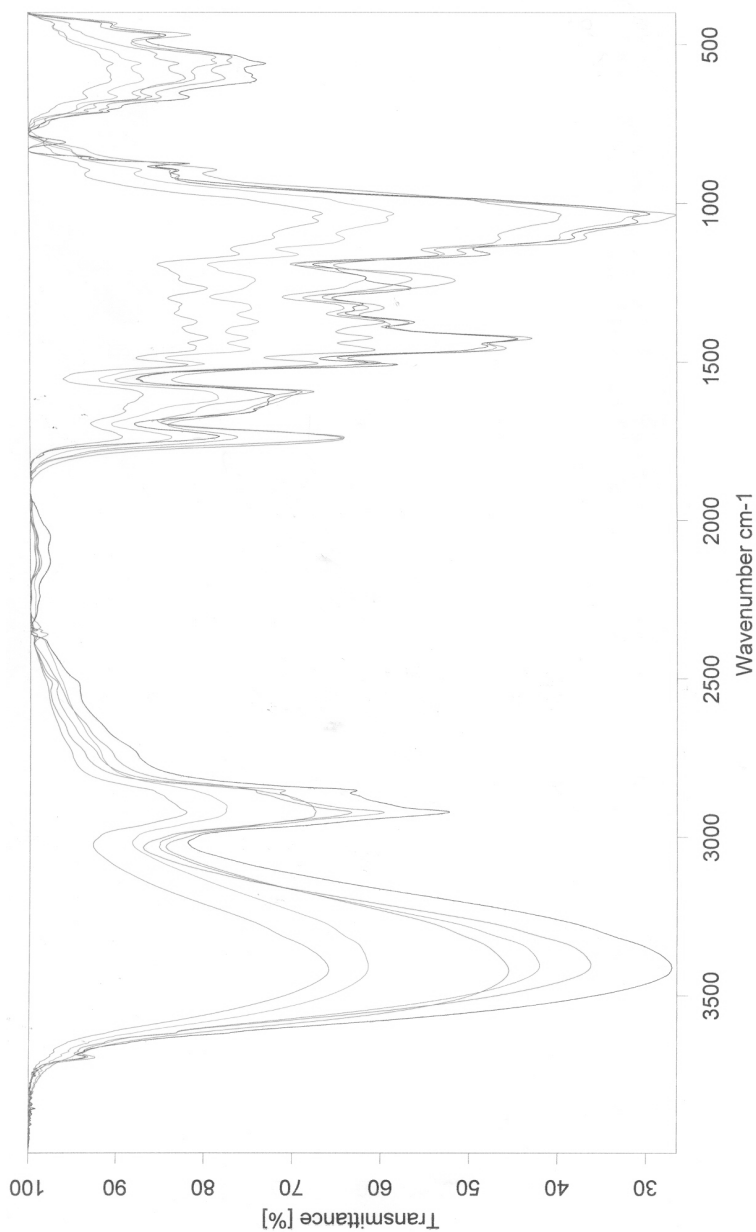
Fig. 2 *FTIR spectra of wood samples.*

The lignin content differs for tree species and decrease with the period of wood use. The 100 years oak has the lowest lignin content and the unused fir the highest. The samples of hardwoods with the same usage duration (40 years), oak and hornbeam have identical lignin content (18.07%).

Table 1 The change in intensity ratios of lignin/carbohydrate (I_{1508}/I_{1375}, I_{1508}/I_{1158})
and carbonyl/carbohydrate peaks (I_{1738}/I_{1375}, I_{1738}/I_{1158})

No	Wood	lignin/carbohydrate ratio		carbonyl/carbohydrate ratio	
		I_{1508}/I_{1375}	I_{1508}/I_{1158}	I_{1738}/I_{1375}	I_{1738}/I_{1158}
1	Fir, 70 years	5.33	2.66	3.66	1.83
2	Fir, new	2.44	1.38	2.78	1.56
3	Oak, 100 years	2.75	0.91	5	1.66
4	Oak, 40 years	2.86	2.22	6.14	4.77
5	Acacia, 50 years	2.6	1.3	3.6	1.8
6	Hornbeam, 40 years	3.33	1.33	7.5	3

Conclusions

FTIR analysis of wood samples is a fast method to identify structural and chemical changes induced by various degradation mechanisms.

Spectra of the different aged tree species show the characteristic bands of lignin and carbohydrates, only small shifts in position and intensity being observed.

The lignin content was determined from the C=C band intensity. The lignin content decreased with the period of usage, this finding being confirmed by the relative change in the ratio lignin/carbohydrate reference bands for oak samples. The lignin content is very low indicating an advanced degree of microbial degradation.

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