Changes of Wood Surfaces Treated with Natural-based Products – Structural and Properties Investigation

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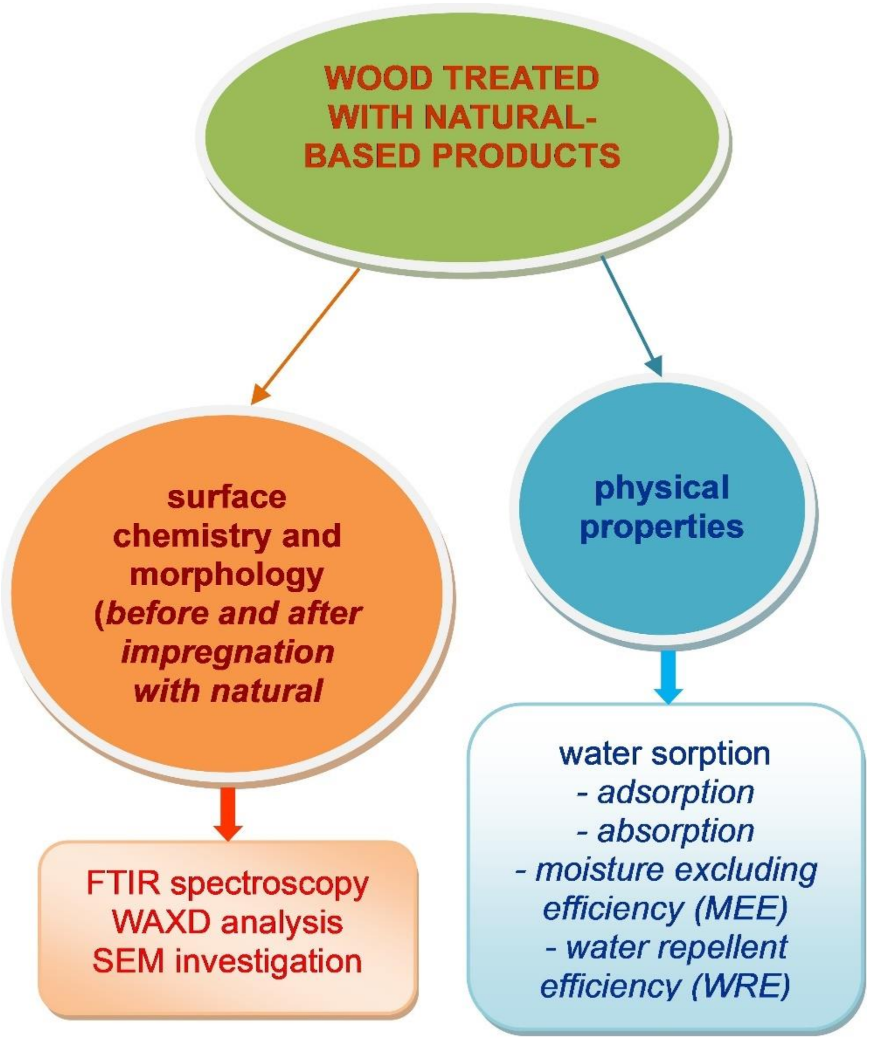
DOI: 10.15376/biores.19.3.5895-5915

GRAPHICAL ABSTRACT



WOOD TREATED WITH NATURAL-BASED PRODUCTS

surface chemistry and morphology (*before and after impregnation with natural*

FTIR spectroscopy
WAXD analysis
SEM investigation

physical properties

water sorption
- *adsorption*
- *absorption*
- *moisture excluding efficiency (MEE)*
- *water repellent efficiency (WRE)*

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Preservative systems based on vegetable seed oils and natural waxes from renewable sources may confer protection to wood under exposure to various environmental conditions. These, as non-toxic substances, can form an environmentally friendly and efficient protective layer on the wood surfaces, with beneficial effects on their water resistance and dimensional stability. Thus, these natural coatings may hinder biodegradation of wood products to a certain degree. In present paper, softwood samples (from *Abies alba* fir tree species), prepared as dried discs (25 to 30 mm diameter, 8 to 10 mm thickness), were surface impregnated by dipping using vegetable oils, namely *Asclepias syriaca* seed oil, and soybean oil, respectively. Beeswax treatment was also applied for comparison purposes. Surface chemistry and morphology, biodegradation process under controlled and simulated natural conditions, and water sorption behavior of wood samples were investigated. Fourier Transform Infrared spectroscopy, X-ray diffraction, and scanning electron microscopy methods were used for investigation of surface changes in wood samples before and after impregnation with natural based products, as well as under biodegradation conditions in soil burial tests.

DOI: 10.15376/biores.19.3.5895-5915

Keywords: Wood; Vegetable oils; Natural wax; Structural investigation; Properties

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INTRODUCTION

Wood is the most commonly used natural composite material, consisting of polysaccharides (cellulose, hemicelluloses), and lignin, an aromatic polymer acting as reinforcing component. The wood preservative industry is interested in finding low-cost and environmentally friendly means for the treatment of the wood. Oil-type wood preservatives are some of the oldest agents with effectiveness for wood products' preservation (treating wood with chemicals or any biochemical compounds to prevent or slow down the deterioration of wood under exposure to environmental factors or wood-degrading organisms). Their use continues in many applications (Barrett *et al.* 1993; Dahlke *et al.* 1995; Derksen *et al.* 1995; Buisman *et al.* 1998; Williams and Feist 1999; Ulvcrona *et al.* 2005).

A possible way to effectively provide wood preservation is by use of vegetable oils or natural waxes such as beeswax. These have different chemical compositions, as related to the saturation degree in chemical bonds: *Asclepias syriaca* seed oil and soybean oil are highly unsaturated, both being liquids at ambient temperature, while beeswax consists mostly of long straight chain hydrocarbons and mineral oil, having excellent water barrier property, and a melting point of about 50 to 70 ºC. Vegetable oils, as well as beeswax, as non-toxic substances, can form an environmentally friendly and efficient protective layer on the surface of the wood samples, thus improving water resistance of wood and its dimensional stability. These natural coatings may provide some protection through hindering biodegradation process of wood products to a certain degree.

Soybean oil represents a biomaterial with an impressive versatility as one of the most sustainable, bio-renewable, abundant and economical alternative to the petroleum-derived products. Usually, beginning from many years ago, its preponderent application was as a drying oil for solventborne alkyd coating resins (Weigal and Walko 2020).The high relevance of soybean oil is strongly related to its key attributes referring to *hydrophobicity* (in relation with improved performance in coatings), *unsaturation level* (the multiple reactive sites present in its structure make it appropriate for various chemical transformations - epoxidation, alcoholysis, transesterification, acidulation, metathesis, isomerization, acrylation and other forms of polymerization -, resulting in polymeric materials with versatility in paints and coatings applications while still maintaining the intrinsic hydrophobicity), and *carbon chain lengths* (the C_{18} carbon chains can provide coating films with improved flexibility and hydrophobicity). Soybean oil may provide many sustainable opportunities for development of crosslinkable resin technology through positive impact upon coatings' properties (*e.g.*, hardness, durability, impact resistance, water repellency) under different tough outdoor conditions of exploitation (heat, moisture) (Ozgenc *et al.* 2013; Olsson *et al.* 2014; Rosu et al. 2016).

Asclepias syriaca (milkweed) seed oil represents 25 to 30% by weight of the seed and has an unusual composition, referring to saturated, monoene, and diene acids of both the C_{16} and C_{18} series (Chisholm and Hopkins 1960; Hopkins and Chisholm 1961). It has potential new uses through conversion of the polyolefinic triacylglycerols component (TAG - the primary storage form of the fatty acids) to the oxiranes and polyhydroxy TAG (Harry-O'kuru 2005). It contains over 90% unsaturated fatty acids with nearly 50% linoleic acid and less than 2% linolenic acid, this offering potential ways for technical applications (Harry-O'kuru *et al.* 2002) including as an alternative source of biodiesel fuel (Holser and Harry-O'Kuru 2006). Despite of increasing interest over the years for this new industrial crop mainly in relation with its floss uses as fiber fill material in hypoallergenic pillows and comforters (Crews *et al.* 1991) or in combination with cotton fibers for woven textiles (Louis and Andrews 1987), the *Asclepias syriaca* plant still remains ubiquitous but underutilized.

Some information about soybean and *Asclepias syriaca* seed oils' chemical composition as fatty acids (Harry-O'Kuru *et al.* 2002; Ivanov *et al.* 2010) are presented in Table 1.

Milkweed seed oil has a different chemical composition from soybean oil, as presented in Table 1 (more oleic acid, almost twice, and linoleic acid; a higher UFA (unsaturated fatty acids)/SFA (saturated fatty acids) value. It has a very low oxidative stability (Holser 2003). It could be a good water repellent due to its viscosity. The unsaturated components are prone to some polymerization processes and generate thin films on wood surfaces in the presence of oxygen from atmosphere.

Natural waxes are a mixture of various long-chain fatty acids and a variety of other chemical constituents, depending on their origin. They have a versatile potential in a multitude of applications in relation with their unique physical and chemical characteristics. In particular, wax from the honeybee (beeswax) is one of the most useful waxes (Tulloch 1970; Tulloch 1971; Tulloch 1980a; Krell 1996; Crane 2009; Tinto *et al.* 2017; Menezes and Athmaselvi 2018).

Table 1. Main Fatty Acids Composition (% w/w) of Soybean Oil and *Asclepias Syriaca* Seed Oil

Fatty Acid		Structure	Soybean Oil	*Asclepias syriaca* Seed Oil
saturated	palmitic	(**C16:0**) $CH_3(CH_2)_{14}COOH$	16.95	5.7
	stearic	(**C18:0**) $CH_3(CH_2)_{16}COOCH_3$	5.15	2.5
unsaturated	oleic	(**C18:1**) $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOCH_3$	16.02	31.0
	linoleic	(**C18:2**) $CH_3(CH_2CH{=}CH)_2(CH_2)_7COOCH_3$	47.57	50.5
	linolenic	(**C18:3**) $CH_3(CH_2CH{=}CH)_3(CH_2)_7COOCH_3$	12.11	1.2
UFA/SFA			**3.42**	**10.08**

Note: Results as mean ± standard deviation (n = 3); SFA - saturated fatty acids; UFA - unsaturated fatty acids

Waxes are usually used as coating material in the wood industry and present advantages such as easiness of application *per se* or in combination with other coating components in different formulations which contribute to wood's appearance (gloss) and softness preservation, alongside conferring hydrophobic properties (Liu *et al.* 2011). The complex chemical composition of waxes is based on mixed long-chain lipophilic compounds with solubility in organic solvents and good dispersion in water. These compounds turn into a liquid state with low viscosity after melting and may constitute a protective coating exhibiting water repellency while preserving the wood initial structure and its appearance (Bulian and Graystone 2009).

Beeswax is a multicomponent material that may or may not be multiphasic, a natural cross-linking polymer referring to wax produced by the honeybee *A. mellifera*. The wax hardens over time (when cold is brittle) and contains a wide variety of compounds including long-chain alkanes, fatty acids, esters, polyesters, and hydroxy esters (Tulloch 1980b; Bonvehi and Bermejo 2012; Polat *et al.* 2013).

Beeswax is an inert material with high plasticity, insolubility in water, resistance to many acids, solubility in most organic solvents and, after warming, in alcohol and fatty oils. When used in coating application, beeswax provides an excellent opportunity for reducing the water vapor permeability of hygroscopic biodegradable materials (Reis *et al.* 2018). A biocidal effect can be exerted through beeswax application on the wood surfaces under exposure to soil burial conditions (Németh *et al.* 2015), as well as improvement in wood dimensional stability and hydrophobic properties (Li *et al.* 2020).

In the present study, softwood samples (from *Abies alba* fir tree species), prepared as dried discs, were surface impregnated by dipping using vegetable oils, namely *Asclepias syriaca* seed oil (coded ASSO), and soybean oil (coded SBO), respectively. Beeswax (BW) treatment was also applied for comparison purposes. Surface chemistry and morphology, biodegradation process under controlled and simulated natural conditions, and water sorption behavior of wood samples were investigated. Fourier Transform Infrared (FTIR) spectroscopy, wide-angle X-ray diffraction (WAXD), and scanning electron microscopy (SEM) methods were used for investigation of surface changes in wood samples before and after impregnation with natural based products, as well as under biodegradation conditions in soil burial tests. The last-mentioned testing was selected for the present work because beeswax melts upon heating. Thus, it is not ideal for outdoor applications. Another reason for this choice is the fact that degradation using underground contact conditions can occur to a higher rate considering the large range of present factors, amongst them the enzymatic ones being the most significant.

EXPERIMENTAL

Samples Preparation

Fir tree wood (*Abies alba* 4 years old), coded as FT, was harvested from the forest in east-northern Romania and provided by a local market. Ten specimens for each treatment were randomly taken from the heartwood part of the fir tree. Prior to the chemical treatment, another ten wood samples were cut and used as control specimens (*i.e.* untreated samples). Thus, both control and treated specimens (a total of 40 samples - ten samples for control and each treatment type) were prepared from the same source of raw wood material.

Vegetable oils, including ASSO, and SBO respectively, were obtained through seed extraction process. ASSO was obtained in laboratory as mentioned in literature data, while SBO had resulted from an industrial process, being supplied by a local store. BW was provided by a local market.

Wood samples as round discs having 25- to 30-mm diameter, 8- to 10-mm thickness were cut and used for experiments. The wood grain direction was perpendicular to the circular surface of the discs. Firstly, wood samples were extracted using a mixture of organic solvents (ethanol/toluene 1/2 ratio) for 8 h in a Soxhlet apparatus, followed by washing with hot distilled water (60 °C). The preliminary solvent extraction of the wood specimens was carried out to eliminate the influence of these extractives on the course of degradation process, since it is well known that the presence of extractives in wood composition can impart resistance to decay in their natural state (Kirker *et al*. 2013). At the same time, the extraction pre-treatment of wood can positively influence its porous structure (Zhao *et al.* 2020). Free-extractives wood samples were further vacuum oven-dried at 70 °C for 24 h. Afterwards, wood specimens with an average moisture content of 7.5% were surface impregnated by dipping using ASSO, SBO, and BW respectively, at 90 °C for 1 h under vigorous stirring. Wood samples were coded FT-C (control), FT-ASSO, FT-SBO, and FT-BW, respectively. All wood samples, both control and treated ones, were further placed in a vacuum oven at 70 ºC for 24 h to achieve constant dry weight values.

Evaluation of Weight Percent Gain for Wood Samples

The efficacy of wood samples treatment was assessed by weight percent gain (WPG) estimation. After impregnation by dipping treatment with vegetable oils and beeswax, the wood samples were removed from reaction vessel, pre-dried at room temperature for 24 h, and subsequently vacuum oven-dried at 70 °C for 24 h until constant weight was obtained. The WPG values were calculated by Eq. 1 from the wood sample dry weight before and after treatment for ten reference specimens (for each treatment type).

$$\text{WPG (\%)} = [(m_{\text{treated}} - m_{\text{untreated}}) / m_{\text{untreated}}] \times 100 \qquad (1)$$

where $m_{\text{untreated}}$ and m_{treated} represent the dry weight of wood samples before and after treatment with vegetable oils and beeswax, respectively.

Soil Burial Tests of Wood Samples

Five treated wood samples for each type of treatment were buried in pots containing garden soil for 365 days under laboratory environmental conditions at 28 °C. The same quantity of water was added in each pot at the same time interval. The untreated wood samples were used as control reference. Wood samples were investigated for evidence structural and properties changes.

FT-IR Spectroscopy Investigation

FTIR spectroscopy of wood specimens was performed on a Bruker FTIR spectrometer (Vertex 70) equipped with the MIRacle ATR accessory designed for single or multi-reflection attenuated total reflectance. Spectra were registered in the range from 500 to 4000 cm^{-1} at a spectral resolution of 4 cm^{-1}, and 64 scans were averaged.

WAXD Analysis

The structure chemistry of wood samples was investigated by wide-angle X-ray diffraction using a Bruker AD8 ADVANCE X-ray diffractometer with Cu $K\alpha$ radiation at 60 kV and 50 mA, at room temperature. Scattered radiation was detected in the diffraction angle 2θ ranging from 10° to 30° at a rate of 2° min^{-1}.

SEM Characterization

Wood samples morphology was analyzed using a scanning electron microscope (FEI QUANTA 200ESEM). Air dried samples were fixed onto aluminium stubs through carbon adhesive disks, and their fractured surface was observed with a low-vacuum secondary electron detector using the accelerating voltage of 25.0 kV. The samples were analysed at room temperature and at an internal pressure of 0.50 torr.

Water Sorption Behavior of Wood Samples Impregnated with Natural-Based Products

Water absorption data were obtained by placing the wood samples in 100 mL glass vessels containing distilled water. Sorption tests were conducted at 27 °C and for immersion periods, from 5 h to about 140 h. The glass vessels were placed in constant-temperature water bath controlled within ± 0.5 °C of the testing temperature. After soaking, the moisture content was calculated based on the increase in the wood sample weight at different times of immersion.

Water adsorption data were obtained by conditioning the wood samples in a desiccator with a higher humidity (a relative humidity RH above 90%), at 25 °C for 100 h. Sodium sulphate was used as desiccant capable of acting as chemically inert drying agent by absorbing water to form crystalline hydrate. The Na_2SO_4 has two stable phases at room temperature: an anhydride, called thenardite, and a decahydrate form, called mirabilite. The last one mentioned phase, as a saturated solution, has an equilibrium relative humidity around 93% (Flatt 2002; Steiger and Asmussen 2008; Donkers *et al.* 2015). Samples were removed at specific time intervals and gently blotted with tissue paper in order to remove the excess of water on the surface. The adsorbed moisture content was calculated based on the increase in the wood sample weight at different times of humidity exposure.

The moisture excluding efficiency (MEE) was calculated as follows (Ahmed *et al.* 2016),

$$\text{MEE (\%)} = [(\text{MCc} - \text{MCt})/\text{MCc}] \times 100 \qquad (2)$$

where MCc represents moisture adsorption of the initial wood sample; MCt is moisture adsorption of the treated wood sample.

Water repellent efficiency (WRE) was determined using the following equation (Adebawo *et al.* 2016),

$$\text{WRE (\%)} = [(W_{\text{untreated}} - W_{\text{treated}})/W_{\text{untreated}}] \times 100 \qquad (3)$$

where $W_{\text{untreated}}$ represents water absorption of the initial wood sample, and W_{treated} is water absorption of the treated wood sample.

RESULTS AND DISCUSSION

Effect of Chemical Treatment on Weight Change of Wood Samples

Weight percent gain values (WPG) were calculated for wood samples under study, and these are presented in Table 2. The differences in behavior for vegetable oils (SBO and ASSO) are in close relation with their chemical structure (ASSO has predominately more unsaturated fatty acids in comparison with SBO) and their viscosity (ASSO has lower viscosity than SBO) which makes ASSO to be better impregnated onto wood samples surfaces (Lanson *et al.* 1945; Holser 2003). Moreover, under heat conditions, ASSO could polymerize and dry somewhat more slowly than SBO. During hot waxing, beeswax penetrates the pores of wood samples and forms on the surface a thin wax film exhibiting some softness after vacuum oven-drying at 70 °C (melting point for beeswax being found between 61 and 67 °C, according to Tulloch and Hoffman 1972).

Table 2. Weight Percent Gain Values (WPG) for Wood Samples under Study

Wood Sample	Weight Percent Gain WPG (%)
FT-SBO	50.50
FT-ASSO	71.80
FT-BW	62.07

FT-IR Spectroscopy Investigation

Evidence of structural changes that occurred in wood samples after treatment with natural based products and degradation under soil contact conditions can be emphasized by means of the FTIR spectral absorbance values ((Hurtubise and Krassig 1960; Nelson and O’Connor 1964; Owen and Thomas 1989; Emandi *et al.* 2011).

Figures 1 through 4 show the FT-IR spectra of FT wood samples as a function of the treatment with vegetable oils and beeswax, initial and after degradation in soil burial tests. These spectra evidenced a peak at 1735 cm^{-1}, which corresponds to the free, non-conjugated carbonyl groups –C=O stretching vibration, the majority occurring in the branched chain of hemicelluloses (mainly ester and acid groups).

The broad peak at 3330 cm^{-1} is associated with –OH stretching vibration from hydrogen bonded –OH group that water and some main wood components (cellulose and hemicelluloses) contain. The peak at 2900 cm^{-1} characterizes C-H stretching in CH_3- and -CH_2- groups. The band at 1630 cm^{-1} is attributed to the water amount present in wood samples. The peak at 1420 cm^{-1} is attributed both to the CH_2 scissoring or symmetric bend in cellulose from wood structure, and to the C=C skeletal vibrations in aromatic ring. The band at 1370 cm^{-1} is ascribed to the C–H deformation (symmetric), and its changes are related to the mass loss of cellulose and hemicelluloses. The peak at 900 cm^{-1} is attributed to the asymmetric out-of-phase ring stretch in the C1–O–C4 glycosidic linkage in cellulose from wood structure (these spectral bands can be suggestive for a more disordered structure when their broadness is observed in the spectra). The peak noticed at 1020 cm^{-1} is assigned to C–O stretch in cellulose and aromatic C–H in-plane deformation plus C–O in primary alcohol. The peak located at 895 cm^{-1} is assigned to C–O–C, C–C=O and C–CH deformation and stretching.

However, there were still slight differences in the bands in the FTIR spectra of samples treated with vegetable oils and beeswax (Vlachos *et al*. 2006; Liu *et al.* 2019; Niu and Song 2021; Tang *et al*. 2021). Vegetable oils are retained on the wood surface by hydrogen bonds between the hydroxyl groups and the ester functional groups in wood polysaccharides. The carbonyl absorption noticed at 1735 cm^{-1} in the FTIR spectra of FT-BW samples did not change after soil burial testing, suggesting that BW and wood only underwent a physical combination, rather than a chemical bonding.

The absorption band for –OH stretching shifted to lower wavenumber values for all wood samples, initial and treated with natural products, after soil burial tests indicating that mostly hydrogen bonds in hemicelluloses and cellulose from the wood structure were broken (these referring mainly to those present between cellulose/hemicelluloses chains) and replaced by hydrogen bonds between cellulose and water molecules (Chauhan and Aggarwal 2004). Considering the preliminary solvent extraction of wood samples, one can expect an increase in wood crystallinity (ethanol-toluene mixture degrades lignin component from wood chemical structure) and a reduction in hydroxyl groups association with increasing free hydroxyl groups content (Sameni *et al.* 2007; Zhao *et al.* 2020).

A decrease for the carbonyl absorption band at 1735 cm^{-1} was noticed for all wood samples, excepting FT-BW ones, after soil contact tests. This was probably due to the water present in soil, this causing the leaching of carbonyl content through degradation processes. BW is an inert, semi-crystalline material with high crystallinity (over 85%) and multi-crystal forms (Kameda 2004). Furthermore, the calculated carbonyl index values are consequently reduced for all wood samples after exposure to soil contact conditions, the lowest values being observed for FT-BW samples.

Hydroxyl groups (–OH) - noticed at about 3350 cm^{-1} (FT-C), 3340 cm^{-1} (FT-SBO, FT-ASSO), and 3375 cm^{-1} (FT-BW) - are the predominant sorption sites linking water with chemical components of wood by means of H-bonds (Engelund *et al.* 2013; Willems 2018; Altgen and Rautkari 2021). Hydroxyl groups content increased for all wood samples during soil burial testing, excepting for those treated with BW when a decrease was observed (an ordering can be given as FT-BW<FT-ASSO<FT-SBO<FT-C). The same evolution was noticed for spectral bands attributed to the moisture (1630 cm^{-1}) that increased for wood samples treated with vegetable oils and FT-C ones, while for FT-BW these values decreased.

The 2925 cm^{-1} and 2854 cm^{-1} bands are attributed to the symmetric stretching vibration of the aliphatic CH_2 group (Vlachos *et al*. 2006). These spectral bands underwent no significant changes but increased in intensity for FT-ASSO and FT-BW samples comparatively with FT-SBO samples, for which these bands presented a clear reduction in intensity. It seems that FT-SBO underwent more chemical composition changes under exposure to soil contact conditions comparatively with FT-ASSO and FT-BW. Moreover, wood samples treated with BW were less affected as chemical changes in comparison with those treated with vegetable oils.

The increase in wood crystallinity for almost all wood samples, after soil burial testing and implicitly under relative high moisture condition, may be explained as crystallization in quasi-crystalline part of amorphous regions due to rearrangement or reorientation of cellulose chains inside these regions (Bhuiyan *et al.* 2000).

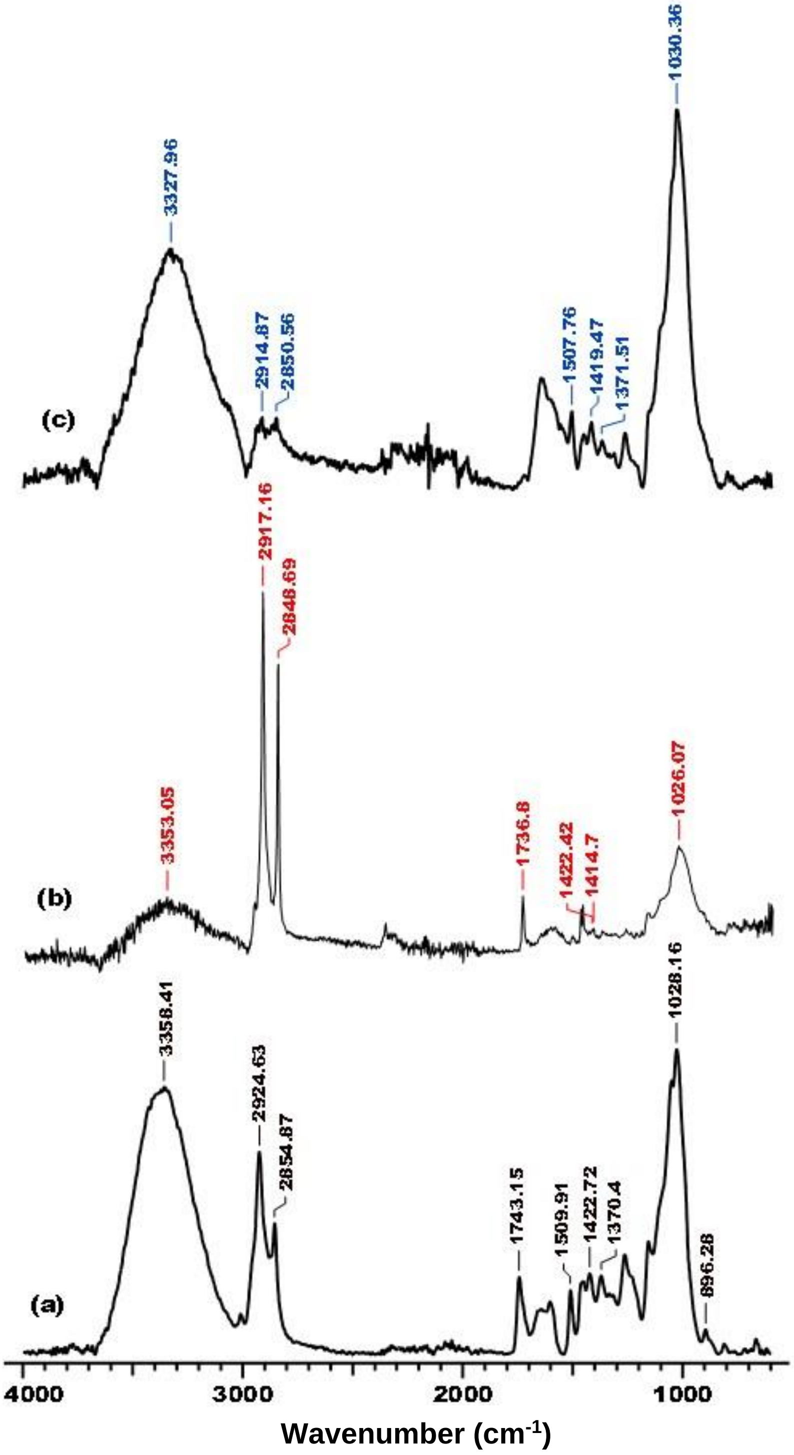


Fig. 1. FTIR-ATR spectra for FT-C samples: (a) initial; (b) after 6 months degradation in soil; (c) after 12 months degradation in soil

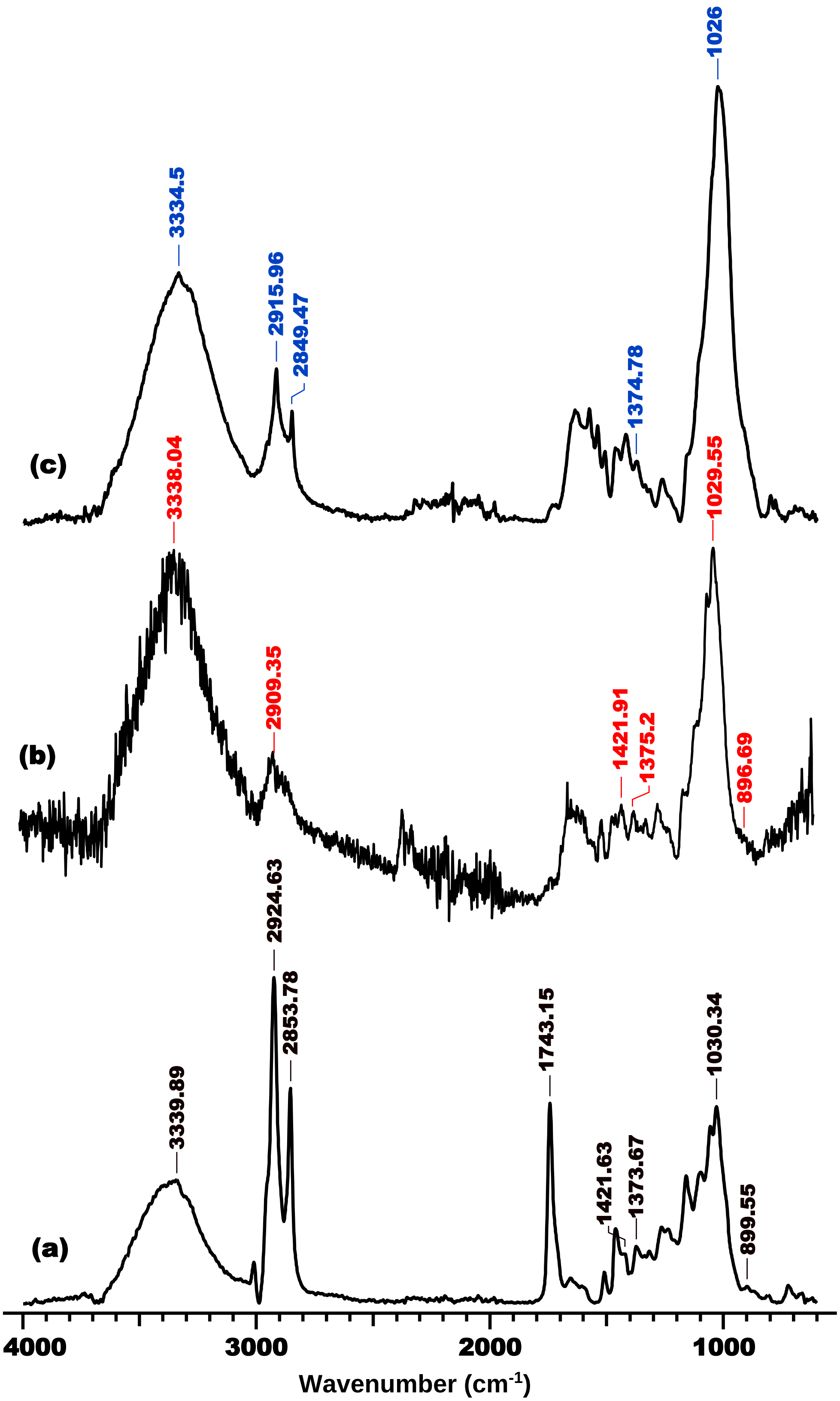


Fig. 2. FTIR-ATR spectra for FT-SBO samples: (a) initial; (b) after 6 months degradation in soil; (c) after 12 months degradation in soil

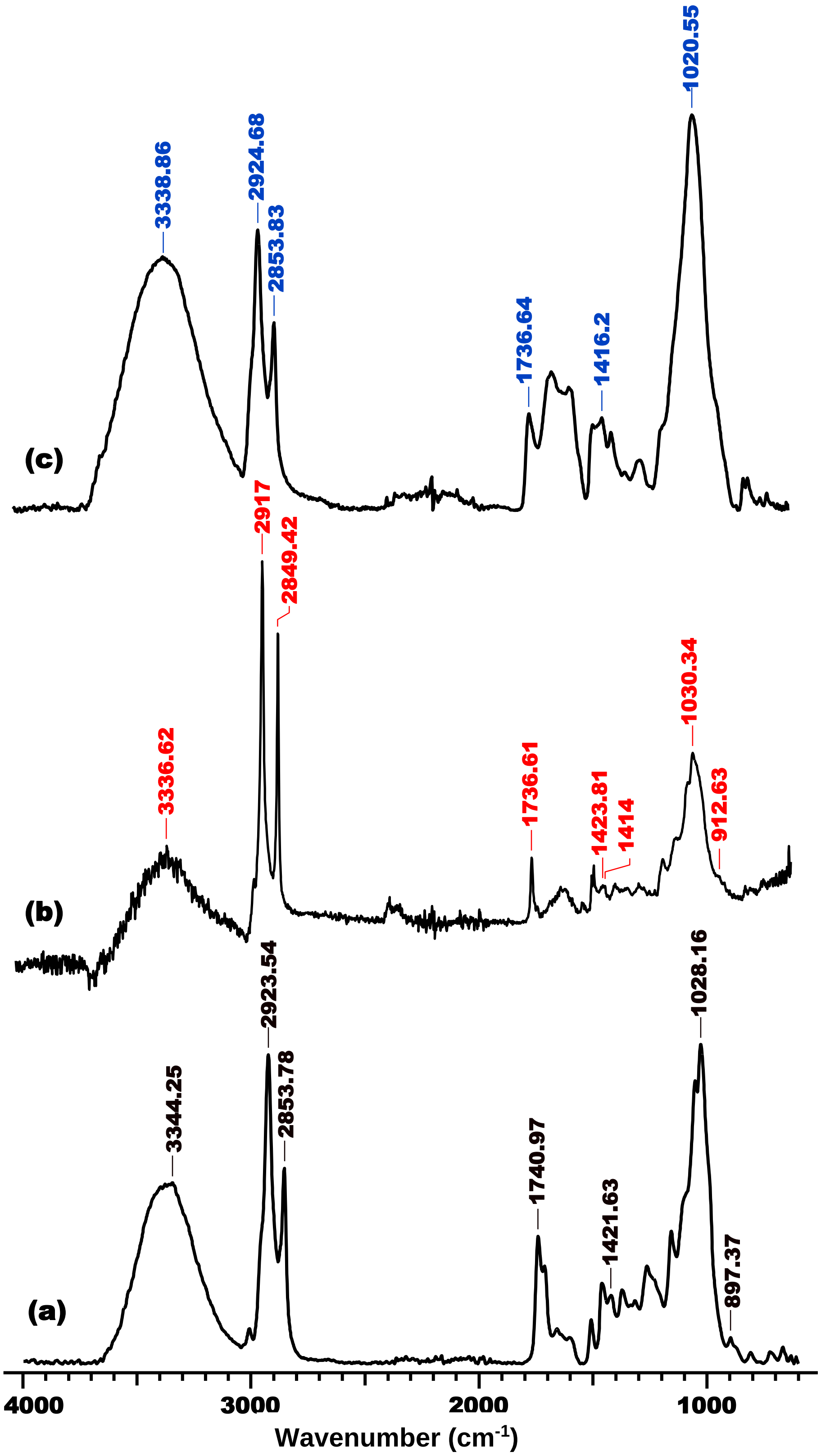


Fig. 3. FTIR-ATR spectra for FT-ASSO samples: (a) initial; (b) after 6 months degradation in soil; (c) after 12 months degradation in soil

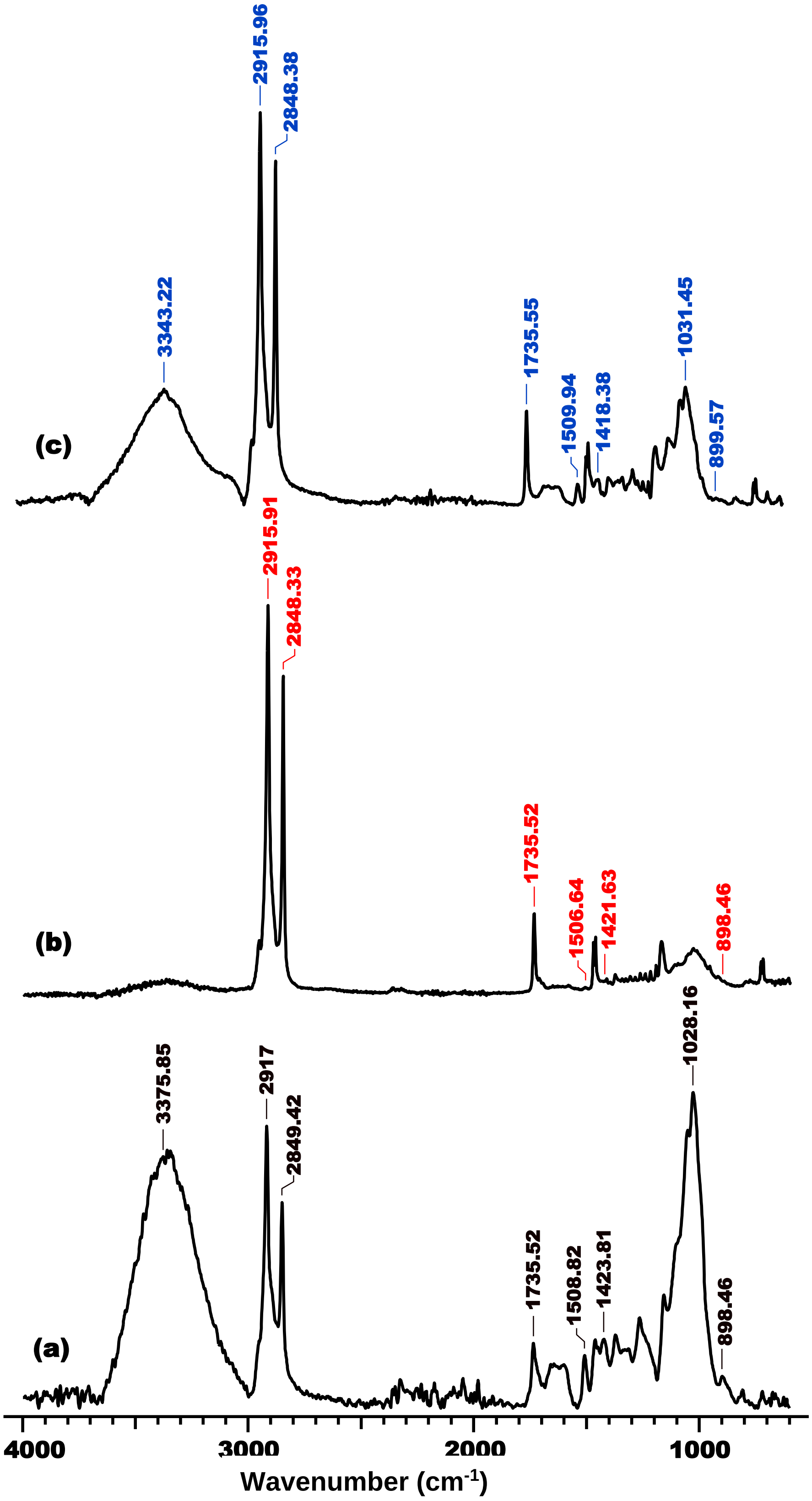


Fig. 4. FTIR-ATR spectra for FT-BW samples: (a) initial; (b) after 6 months degradation in soil; (c) after 12 months degradation in soil

An exception was observed for FT-BW samples, probably due to the affinity of soil's microbial community towards BW's presence on the wood surface, this being an all-natural product that, as most of the water repellents, does not exhibit a biocidal effect and can be digested together with wood.

Furthermore, the relative high moisture condition in wood samples' surrounding soil environment may affect the dynamics of hydrogen bonds (intermolecular H-bonds are easily exchanged in water) (Wohlert *et al*. 2022).

Moreover, the more crystallization in wood cellulose may be related to the particular behavior of hemicelluloses; it is well known that xylan and mannan (the main hemicelluloses components) can crystallize (Yundt 1949; Marchessault and Liang 1962) after occurrence of inherent degradation processes (*e.g.* depolymerization, release of acidic components). In softwood species, O-acetyl-galactoglucomannan is the principal hemicellulose component, while the xylan component - arabino-(4-O-methyl-glucurono) xylan- does not contain acetyl groups and is more highly branched and more acidic.

Water Sorption Behavior

Wood in the living tree is formed and functions in an essentially water-saturated environment. Wood-water interactions are of real significance and omnipresent, since water affects many important characteristics of wood when considering its valorization for more increasing societal demands (Chauhan and Aggarwal 2004; Thybring *et al*. 2022).
Wood can absorb significant amounts of water in its structure (both within cell walls and in the porous, macro-void structure) from surrounding environment through two different mechanisms, namely adsorption and absorption (Skaar 1988; Malmquist and Söderström 1996). Physical sorption, related to swelling and shrinkage of wood, is always coupled together with the chemical sorption of water to the free OH-groups from wood polymer components. In relation with water adsorption, wood may be viewed as a "swelling gel" (Pidgeon and Maass 1930). The process begins from the wood surface (at low moisture content, water is adsorbed mainly within hemicellulose component) to deeply filling up the structural pores as the level of moisture is increasing. The region of preferential water adsorption, in particular at higher moisture content, is represented by the interface between the crystalline cellulose and amorphous hemicelluloses (Kulasinski *et al*. 2015). In absorption, water molecules are drawn into the permeable wood pores by sponge-like processes through phenomena including diffusion and osmosis, followed by capillary condensation.

In Figs. 5 and 6, water sorption properties by means of adsorption and absorption testing for wood samples after impregnation treatment with vegetable oils, and beeswax, respectively, are presented. The hydrophobic effect induced by the beeswax when it is applied on the wood surfaces was more significant in comparison with vegetable oils. The efficiency of beeswax as hindering agent for moisture sorption processes is also evidenced by the water repellent efficiency (WRE) values that are given in Table 3.

The water uptake curves of wood samples treated with vegetable oils and beeswax were similar to untreated wood, showing an obvious logarithmic shape. The water uptake was faster up to 45 h (as observed in adsorption testing – see Fig. 5) and up to 70 h (as observed in absorption testing - see Fig. 6), and the rate then decreased for water sorption processes. The water sorption extents noticed for FT-BW samples were the lowest in comparison with FT-SBO and FT-ASSO samples, as evidenced by Figs. 5 and 6.

An increasing order for water sorption properties can be represented as:
FT-BW < FT-ASSO < FT-SBO < FT-C.

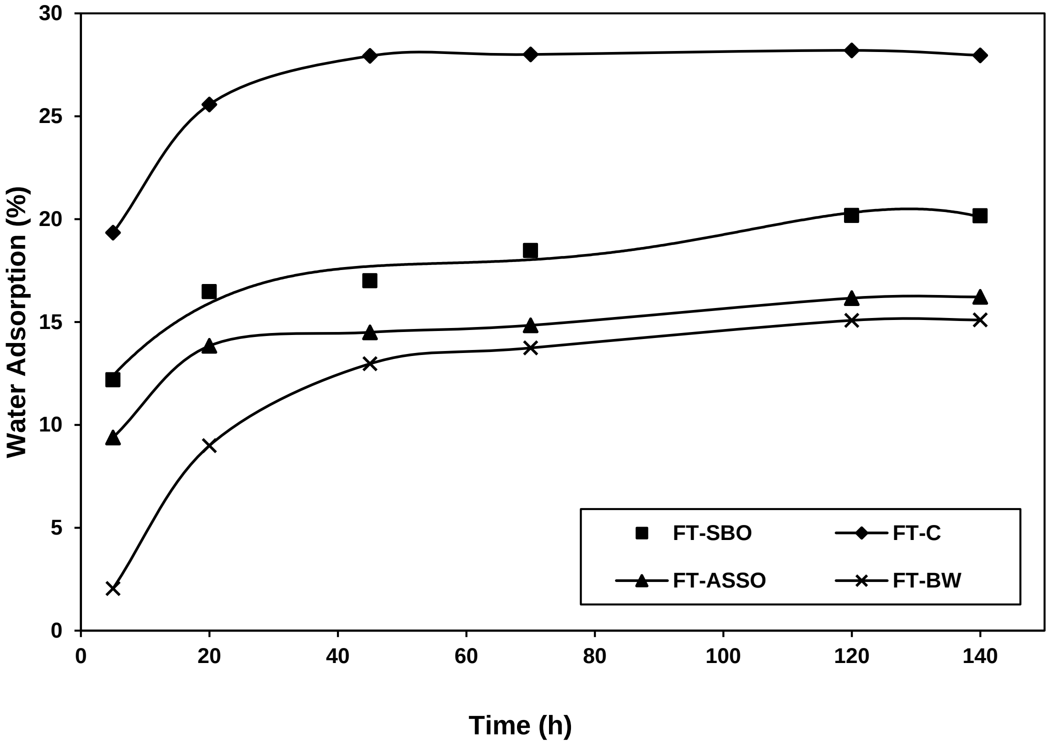


Fig. 5. Water adsorption data for softwood samples (kept in the desiccator under 95% RH conditions and weighed at different time periods)

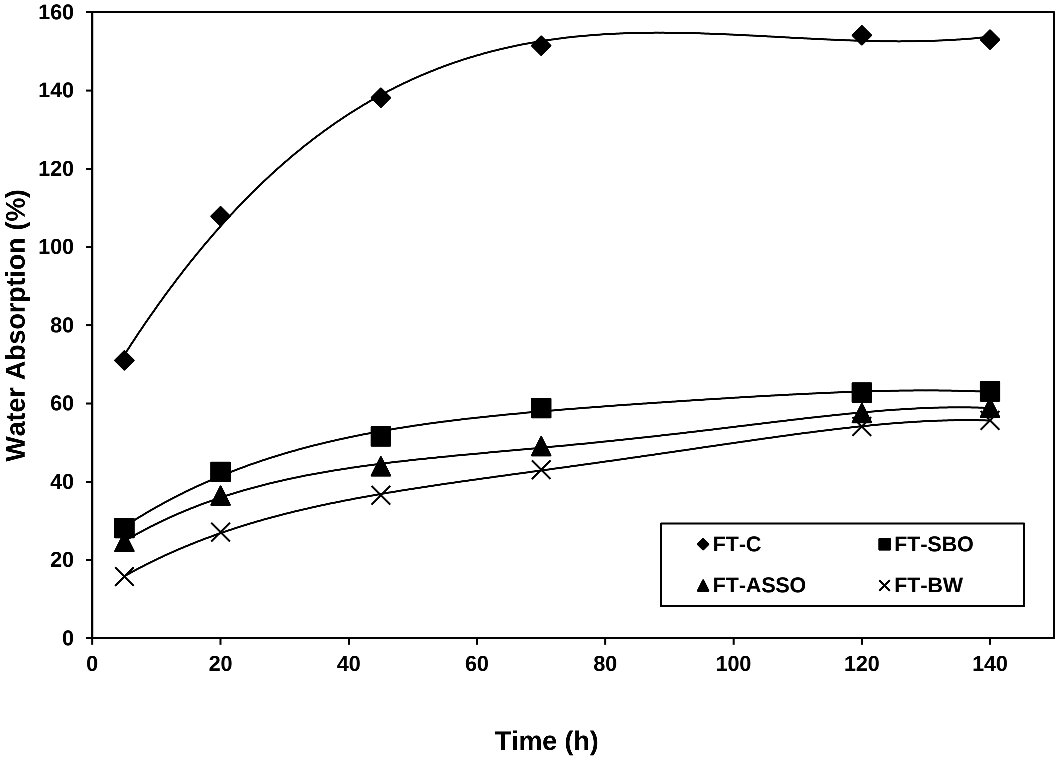


Fig. 6. Water absorption data for softwood samples (immersed in distilled water at constant temperature of 27 °C and weighed at different time periods)

Table 3. WRE Values (%) for Wood Samples Coated with Natural-Based Products

Immersion Time	5 h	20 h	45 h	70 h	120 h	140 h
FT-SBO	60.38	60.57	62.66	61.16	59.27	58.78
FT-ASSO	65.32	66.18	68.19	67.58	62.64	61.51
FT-BW	77.81	74.85	73.55	71.55	64.89	63.62

The moisture excluding efficiency (MEE) was tabulated to explain the hydrophobicity of treated wood measured at 95% RH (Table 4). In the same ambient condition, wood impregnated with beeswax oil absorbed less moisture than wood impregnated using vegetable oils, and thus had improved MEE. Higher MEE values mean higher hydrophobicity. Beeswax treatment reduced the tendency of the wood to take in moisture (related to the degree of water repellency and hydrophobicity) to a greater extent than vegetable oils did, the effectiveness of treatments being in order BW > ASSO > SBO.

Table 4. MEE Values (%) for Wood Samples Coated with Natural-Based Products

Conditioning at 95% RH	5 h	20 h	45 h	70 h	120 h	140 h
FT-SBO	36.97	35.58	39.13	34.03	28.47	27.89
FT-ASSO	51.46	45.87	48.08	47	42.69	41.98
FT-BW	89.40	64.84	53.56	50.93	46.53	45.99

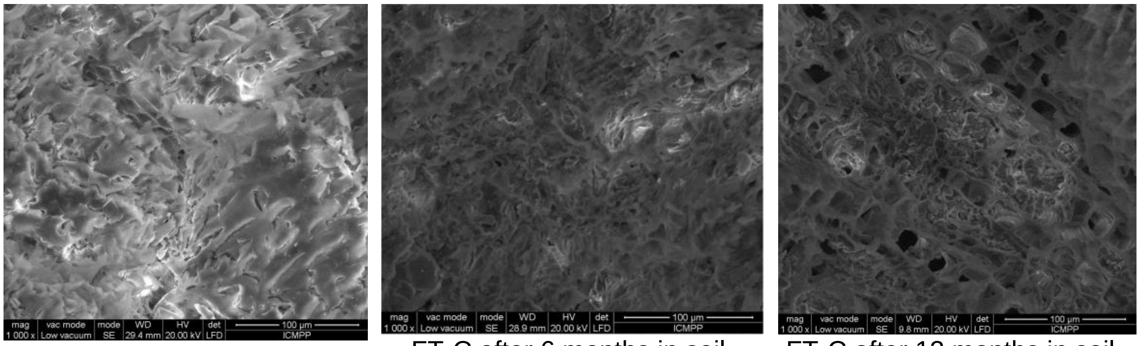
SEM Characterization

Vegetable oils and beeswax used for impregnation penetrated cell walls of wood samples to a certain depth as evidenced by SEM. Microscopic images (SEM) presented in in Fig. 7 show the distribution of vegetable oils and beeswax in the internal structure of wood samples, initial and after exposure to soil contact conditions. After 365 days of soil contact, wood samples presented significant color changes (darkening) and deterioration in their structural integrity, namely increased brittleness of wood surfaces with occurrence of cracking, mostly for control samples and those impregnated with vegetable oils.

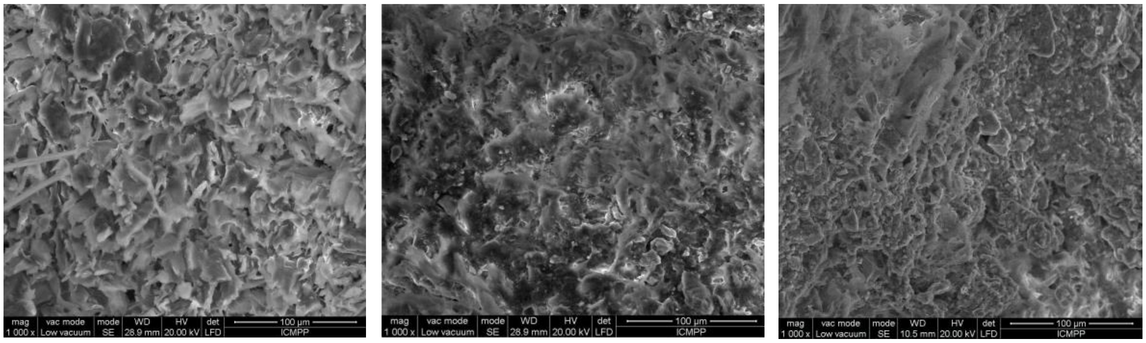
As one can observe, beeswax provided a different protection comparatively with vegetable oils. It had a smaller impregnation depth, but it filled the natural pores of the wood structure, conferring resistance to moisture, with further a more reduced weight loss for wood samples under soil exposure conditions in comparison with those impregnated with vegetable oils (see Table 5). Beeswax was able to act as a physical barrier (as a seal) and has no biocidal effect, these explaining the lower decomposition, expressed as reduced weight loss, of the FT-BW samples comparatively with FT-SBO and FT-ASSO samples.

Table 5. Weight Loss in Wood Samples Exposed to Soil Burial Conditions

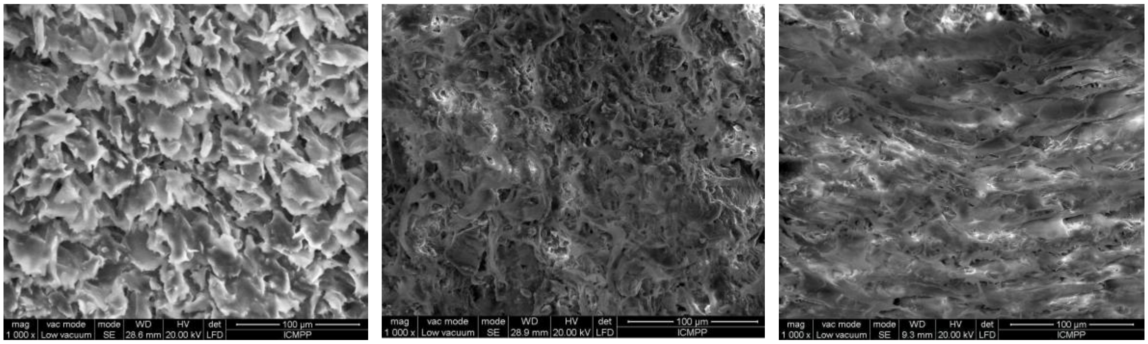
Sample	Weight Loss After 6 Months in Soil (%)	Weight Loss After 12 Months in Soil (%)
FT-C	0.382	17.67
FT-SBO	29.95	47.51
FT-ASSO	34.36	63.32
FT-BW	8.58	8.70



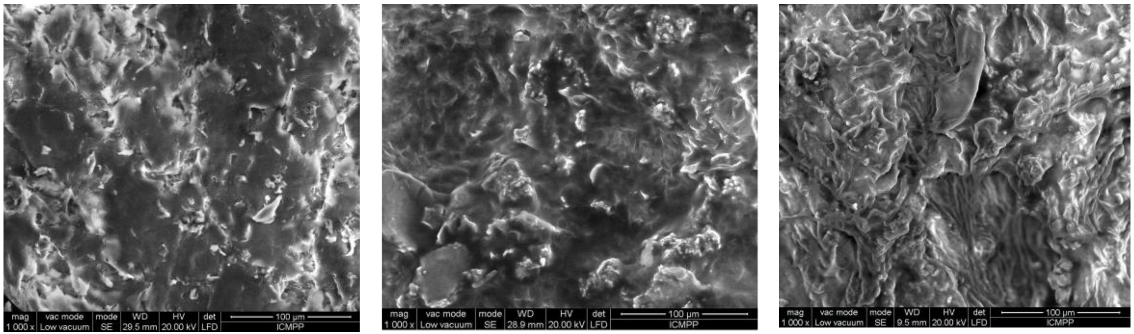
FT-C FT-C after 6 months in soil FT-C after 12 months in soil



FT-SBO FT-SBO after 6 months in soil FT-SBO after 12 months in soil



FT-ASSO FT-ASSO after 6 months in soil FT-ASSO after 12 months in soil



FT-BW FT-BW after 6 months in soil FT-BW after 12 months in soil

Fig. 7. Scanning electron micrographs registered for softwood samples, initial and after burial soil degradation testing

WAXD Analysis

The crystallinity of wood samples, control and impregnated with natural products, was investigated using X-ray diffraction method. Data resulted from X-ray analysis, performed on the wood samples' surface, are given in Fig. 8.

The WAXD pattern of the FT-C sample presents a maximum diffraction peak of the (002) crystal plane of cellulose from wood structure near $2\theta = 21°$, and a diffraction peak around 18° that is specific to the amorphous region. The WAXD patterns of the FT-BW sample evidence the characteristic peaks of beeswax at $2\theta = 21.4°$ and 23.8° (Gaillard *et al.* 2011), the first one overlapping over that specific to wood cellulose component. These peaks are more intense at the end of exposure to soil contact conditions. Overall, these patterns evidence the high degree of crystallinity for wood impregnated with beeswax.

The WAXD patterns for wood samples impregnated with vegetable oils are similar in appearance with those for initial wood samples, the peaks being more specific to wood crystalline polymer components. The most intense diffraction peaks were observed for the FT-ASSO samples in comparison with FT-SBO samples.

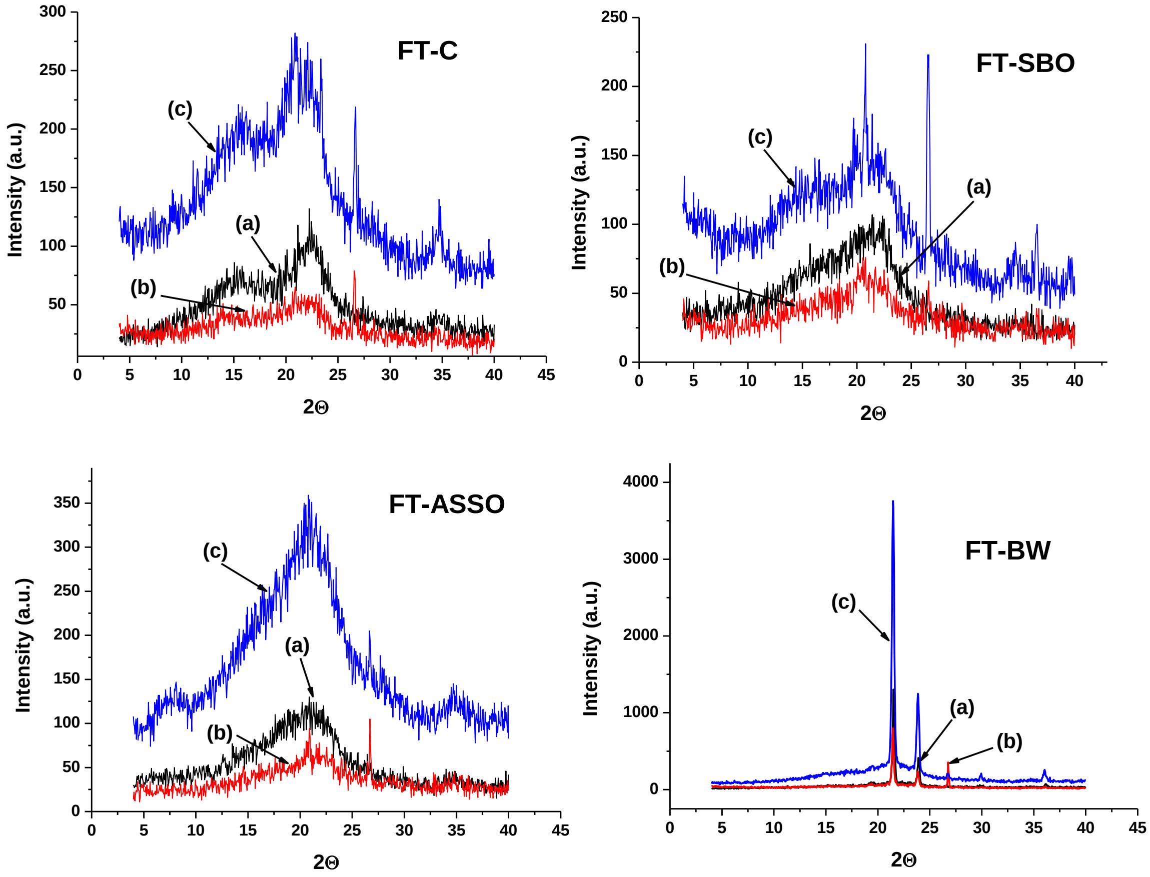


Fig. 8. X-ray diffraction curves recorded for wood samples: (a) initial; (b) after 6 months degradation in soil; (c) after 12 months degradation in soil

CONCLUSIONS

1. Oil-type wood preservatives are some of the oldest preservatives, and their use continues in many applications. A possible way for wood preservation can be provided by use of natural based products such as vegetable oils and waxes (*e.g.*, beeswax) when a significant weight percent gain increase (50 to 72%) can be achieved.

2. After such impregnation tests, a reduction in both moisture adsorption and water absorption values can be noticed for wood samples considered here. The surface hydrophobicity of wood was remarkably improved mostly by beeswax impregnation.
3. Overall, the beeswax treatment reduced the tendency of the wood to take in moisture (related to the degree of water repellency and hydrophobicity expressed as moisture excluding efficiency) to a greater extent than vegetable oils did, the effectiveness of treatments being in order beeswax > *Asclepias syriaca* seed oil > soybean oil.
4. Structural changes of wood samples, untreated and treated, after soil contact testing for different periods of exposure (6 and 12 months), were evidenced by FTIR spectroscopy and SEM investigations. Wood samples impregnated with soybean oil underwent more chemical composition changes under exposure to soil contact conditions comparatively with wood samples impregnated with *Asclepias syriaca* seed oil and beeswax. Moreover, wood samples treated with beeswax were less affected as chemical changes in comparison with those treated with vegetable oils.
5. A loss in weight over 30% for wood samples impregnated with vegetable oils was also noticed. Beeswax can act as a physical barrier and has no biocidal effect. This explains the lower decomposition, expressed as reduced weight loss, for wood samples impregnated with beeswax.
6. Wide angle X-ray diffraction analysis evidenced the crystallinity changes in wood samples, initial and impregnated with natural based products, during exposure to soil contact conditions. A higher degree of crystallinity for wood impregnated with beeswax was observed, but also to a lesser extent for the other wood samples under study, mostly after exposure to soil contact conditions. This evolution may be related to possible crystallization in quasi-crystalline part of amorphous regions due to rearrangement or reorientation of cellulose chains inside these regions under relative high moisture conditions.

ACKNOWLEDGMENTS

The authors dedicate this paper to the memory of their dear colleague and friend, Dr. Ruxanda Bodîrlău, who passed away on June 26th, 2016, and honor her demure support and enthusiastic work. The authors also acknowledge the significant contribution of Eng. Elena Marlică as concerns the WAXD analysis.

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Article submitted: May 2, 2024; Peer review completed: May 18, 2024; Revised version received and accepted: June 30, 2024; Published: July 15, 2024.
DOI: 10.15376/biores.19.3.5895-5915