Studying and imparting moisture absorption qualities of the new wood based bio-composite material

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Abstract. The paper reviews the method of creating a new bio-composite material based on birch wood and describes the mechanism of interaction of used motor oil with birch wood by infrared spectroscopy involved. It also provides data on the moisture absorption of the newly obtained composite. Used motor oil has high hydrophobic and antiseptic properties. The main chemical changes in oils occur as a result of its oxidation during engine operation under the temperature influence. However, the spectrum of spent engine oil is distinguished by the appearance of three new peaks: the wide peak of 3600-3000 cm⁻¹, which is formed during characteristic vibrations of the OH group, indicating water cut in the engine oil, a narrow peak of 1740 cm⁻¹, characteristic of stretching vibrations of the carbonyl group (C = O). In addition to these peaks, the other peak was detected at the 1150 cm⁻¹ frequency and, yet, another weakly pronounced peak of 970 cm⁻¹, which correspond to stretching vibrations of the peroxide group (C-O-O). The mechanism for impregnating wood with used engine oil has been developed. The moisture absorption of wood impregnated with spent engine oil is 3 times less than that of natural wood.

1. Introduction

Forests of the Voronezh region in the forest-steppe part of the forest region occupy 72.6%. The steppe part accounts for 27.4%. Of these, soft-leaved breeds make up 17.5%. Wood is a multifunctional self-organized system with a composite structure and adaptive properties. It is compatible with polymeric, organic, inorganic, metal compounds and systems based on them; it is also capable of forming various families of the new generation composite materials.

In recent years, the interest to applying various species of wood for creating new composite materials with improved physicochemical properties has significantly increased [1-3]. As a rule, composites are heterogeneous systems consisting of one or more discontinuous phases inside of the
matrix [4]. In order to control the properties of the composite various types of fillers are added to the matrix [5]. This paper studied birch wood as a matrix material and spent engine oil as a filler. As a rule, most of the common approaches to wood modification such as chemical, thermal, thermochemical, thermomechanical and others are based on impregnation [6]. Chemical modification of wood creates the possibility for the covalent bond between the functional groups of modifying compounds and the reaction part of the cell wall of wood. Large number of papers [7] study chemical modification of wood attempting to improve its moisture absorption and dimensional stability. Chemical modification helps to increase destruction resistance of wood by reducing the equilibrium moisture content. In order to improve the properties of wood, various oil-based impregnating compositions are applied: various vegetable oils [8] are used for impregnation. The authors [9, 10] modified the studied wood matrix with emulsions based on vegetable oils to impart water-repellent properties to the wood and protect it from UV radiation. The paper studied the possibility to obtain the new type material based on wood modification with glycerol followed by its polymerization with citric acid. The authors indicate the appearance of chemical interaction of wood with a filler, studied by IR spectroscopy, accompanied by vibration frequencies ranging from 2000 to 1500 cm⁻¹ and corresponding to the C-O functional group, as well as the 1720 cm⁻¹ peak, which characterizes the increase in ester bonds within the glycerol-based polymer.

Recently, the attention to utilization of spent engine oils (SEO) has increased due to the ever-growing amounts of cars in Russia. One of the possibilities to dispose the SEOs is using them for wood impregnation in order to impart hydrophobicity and antiseptic qualities to this material. All modern engine oils consist of basic oils and additives that improve their properties [11]. Hydrocarbons and their mixtures are usually used as base mineral oils [12, 13]. In engine oil, the basic oil is 86%, whereas the rest of the compound comprises 1% of zinc dialkyldithiophosphate as corrosion inhibitor, 4% of both barium and calcium sulfonates as detergent additives, 4% of polymethyl methacrylate as multifunctional additive, and polyisobutylene as viscosity modifier [14]. Organic compounds predominant in used oils have not been determined as of yet. Nevertheless, several classes of compounds that are usually observed in used oils have been identified as aliphatic compounds and structures of mono-, di-, and tri-polyaromatic rings. Aliphatic compounds comprise about 73-80% of the total volume of spent oil [15]. This fraction consists of alkanes and cycloalkanes (1-6 rings). Respectively, mono- and diaromatic compounds account for 11-15% and 2-5% of the total volume of spent oil. The main chemical changes in oils occur as a result of oxidation caused by heating.

According to the researchers [16] spent engine oil has high hydrophobic and antiseptic properties and can modify the wood matrix. Wood species is one of the main factors determining the degree of absorption of the impregnating composition [17]. Specific location of the cell walls results in more intensive impregnation of wood substance in the longitudinal direction as compared to radial or tangential directions.

The purpose of the work is to create a new bio-composite material based on wood, to establish a mechanism for the interaction of used motor oil with birch wood by FT-IR spectroscopy, and to study the moisture absorption of the composite received.

2. Methods and materials
For experimental investigation wood samples from birch wood (Betula pendula) were prepared. For this, 25-year-old birch wood tree was cut down in a training experimental forestry farm of Voronezh State University of Forestry and Technologies, Voronezh area, Russian Federation, and 20x20 mm size wood samples, with 10 mm height along the fibers, were cut out from the central part of wood
trunk in radial and tangential directions. Produced samples were dried in an oven at 103±2 °C at ambient pressure until 12% of wood moisture.

Samples were sawn on a miter saw METABO KGS 315 Plus (Metabo, Germany, 2012) at 4100 rpm and then used for moisture absorption studies.

The amount of impregnating composition absorbed (%) determined by the change of mass before and after impregnation.

Motor mineral oil 10W-40 and semi-synthetic motor oil 10W-40 produced by LLC LLK-International company and used motor oil based on initial distillate oil purchased from LLC Aurora, firms LUKOIL, year of manufacture - 2018. Auto were used for FT-IR spectroscopic analysis.

The moisture absorption of birch samples of 20 × 20 × 10 mm in size was determined on dried samples placed in special test tubes with corks at 103 ± 2°C temperature and brought to the completely dry state. Then, the samples were placed in a desiccator filled with distilled water above the level of the insert, and the samples were lowered under the desiccator insert. Two desiccators were filled with distilled water: one of the tubes contained the samples of natural wood, and the other contained the samples with impregnated spent oil. The amount of absorbed moisture was calculated by the following formula (1):

\[ W = \frac{m_n - m_1}{m} \cdot 100\% \]  

Whereas: \(m_n\) is the weight of the test tube containing samples (in grams); \(m_1\) is the weight of the test tube containing the sample in completely dry state, (in grams); \(m\) is the weight of the test tube, (in grams); weighing of the samples was carried out after 1, 2, 3, 6, 9, 13, 20, and 30 days.

Wood impregnation was done applying the method of hot-cold baths, the modes of which is described in details in [16].

Samples were weighted after 1, 2, 3, 6, 9, 13, 20, 30 days.

IR studies were done using FTIR-spectrometer Bruker VERTEX 70 (Bruker, Germany, 2007), which provides registration of IR spectra in the range of 400-4000 cm⁻¹ on the broken total internal reflection with diamond prism, which allows to obtain spectra in the middle IR range for organic, inorganic, composite and other samples in liquid and solid state. For current study wood samples were taken from the interior middle part of wood. IR absorption spectra allows determining functional groups of different samples. This method is highly sensitive and makes it possible to analyze substances in any physical state that is especially important while studying insoluble compounds, such as wood and products of its modification.

3. Results and discussion
Following the results of FT-IR spectroscopic analysis of birch wood (figure 1), the presence of O-H band absorption at 3350 cm⁻¹ frequency was established due to the formation of a hydrogen bond between the hydroxyl groups of linear cellulose molecules and oxygen atoms involving proton donor and proton acceptor interactions [18]. Weak peaks of 2923 and 2853 cm⁻¹ frequencies are observed; this area is characterized by symmetric and asymmetric C – H stretching vibrations in methyl and methylene groups [19]. The 1594 cm⁻¹ band corresponds to the stretching vibrations of the benzene ring of lignin (figure 1) [20]. The spectrum contains weakly pronounced absorption bands ranging from 1594 cm⁻¹ and 1375 cm⁻¹, which are attributed to skeletal vibrations of the aromatic ring. In the 1150–1000 cm⁻¹ area absorption bands of stretching vibrations of C – O bonds, typical for primary, secondary, and tertiary hydroxyl groups, appear [21].
We studied the FT-IR spectra of mineral, semisynthetic, and used motor oils (SEO) shown in figure 2. The functional groups of mineral motor oil were compared with the SEO groups. As a result, the presence of new bonds of various nature with birch wood was determined.

All modern engine oils consist of base oils and additives that improve their properties [22]. Hydrocarbons and their mixtures are usually used as base mineral oils [23]. Synthetic oils consist of synthetic hydrocarbons - polyalphaolefins, glycols, organopolysiloxanes and esters. In engine oil, the base oil comprises 86%, a corrosion inhibitor zinc dialkyldithiophosphate comprises 1%, detergent additives barium and calcium sulfonates comprise 4%, multifunctional additives polymethyl methacrylate comprise 4%. Viscosity modifiers (polyisobutylene) are used as additives. Organic compounds predominant in used oils have not yet been determined. Nevertheless, several classes of compounds that are usually present in the composition of used oils have been identified, namely, the aliphatic compounds and structures of mono-, di-, tri-polyaromatic rings. Aliphatic compounds make up approximately 73-80% of weight of the used oil. This fraction consists of alkanes and cycloalkanes (1-6 rings). The main chemical changes in oils occur as a result of oxidation during engine operation under the influence of heating. During oxidation, paraffin hydrocarbons are converted to hydroperoxides, which decompose to water and ketone with the subsequent formation of carboxylic acid and aldehyde.

In modern society, the problem of recycling of used motor oils is crucial. Its amount has risen sharply over the past decade and tends to subsequently increase. One of the possibilities to dispose the used motor oils is to use them as an impregnating composition for wood in order to improve the quality of wood by imparting it with hydrophobic and antiseptic qualities. In general, motor oils contain some small amount of gasoline, additives in the form of synthetic detergents, dispersants, oxidation inhibitors, corrosion inhibitors and additives, as well as N-, S-compounds, metals (Pb, Zn, Ca, Ba, Mg) and a wide range of aromatic and aliphatic hydrocarbons with long chains (C15-C50). Organic compounds predominant in used oils have not yet been determined. Nevertheless, several

![Figure 1. FT-IR spectrum of Natural Birch Wood.](image-url)
classes of compounds that are usually present in waste oils have been identified: aliphatic compounds and structures of mono-, di-, tri-, polycyclic aromatic rings.

This spectrum is characterized by the presence of a well-pronounced two-humped peak at an absorption frequency of 2925 cm\(^{-1}\), corresponding to stretching vibrations of the CH group of alkanes, and 2850 cm\(^{-1}\) vibrations of CH of methyl ethers.

The absorption bands of 1460 cm\(^{-1}\) and 1380 cm\(^{-1}\) correspond to vibrations of the methyl group, whereas content of methylene groups of CH\(_2\) is determined by the band of 720 cm\(^{-1}\).

Figure 2. FT-IR spectra of mineral, semi-synthetic and spent motor oils.

The IR spectra of mineral and semi-synthetic oils are identical. However, the spectrum of used motor oil is distinguished by the appearance of three new peaks: a wide peak of 3600-3000 cm\(^{-1}\), which is formed during characteristic vibrations of the OH group, indicating water cut in the engine oil, a narrow peak of 1740 cm\(^{-1}\), characteristic of the stretching vibrations of the carbonyl group (C=O). In addition to these peaks, the peak was detected at a frequency of 1150 cm\(^{-1}\) and a weakly pronounced peak of 970 cm\(^{-1}\), which correspond to stretching vibrations of the -C-O-O- peroxide group. This group appears during the oxidation of hydrocarbons as a result of the oil's engine operation. Confirmation of the possibility of the appearance of peroxides can be found in the work of Academician A. N. Bach, who discovered the presence of peroxide compounds with high excess energy as the primary products of hydrocarbon oxidation. Under certain conditions, the exothermic decomposition of peroxides occurs according to the ‘chain mechanism’ proposed by the Academician and Nobel Prize winner N.N. Semenov. The formation of all the primary molecular oxidation products is preceded by the formation of peroxide radicals.

Impregnation of SEO birch wood on the FT-IR spectra reveals distinct bands characteristic of the FT-IR spectrum of SEO and birch wood: bands 2925, 2850 (stretching vibrations of the CH group), peaks 1380 cm\(^{-1}\) and 1460 cm\(^{-1}\) corresponding to vibrations of the CH\(_2\) group. Peaks characteristic of birch wood and UMO are retained: 1735 cm\(^{-1}\) (group C=O). However, its intensity decreases. We observe the band 1595 cm\(^{-1}\), characteristic of the benzene ring of lignin with a slight decrease in the
absorption intensity. The peak of 1235 cm\(^{-1}\) corresponds to a group of phenols, the value of which is much larger in all types of wood and increases even more in impregnated wood (figure 3).

![Figure 3. FT-IR spectra of SEO, impregnated wood, natural wood.](image)

On the FT-IR spectrum of birch impregnated with SEO, there is no peak at 1150 cm\(^{-1}\) (CH\(_2\) group) as a result of oxidation of hydrocarbons and the formation of peroxides, the absorption frequency of which is 720 cm\(^{-1}\).

Peak 3350 cm\(^{-1}\) absorption band in natural wood corresponds to the oscillation frequency of O-H groups. This band in the SEO impregnated sample decreases due to its shifting to lower frequencies (by 50 cm\(^{-1}\)) and the participation of these groups in the formation of the hydrogen bond. The transition of a water molecule from its main vibrational state to an excited one corresponds to an infrared band of 1594 cm\(^{-1}\).

In the course of transition from water monomers to dimers and trimers, the maximum absorption of stretching vibrations of the O-H bond shifts to lower frequencies. On the contrary, for deformation vibrations H-O-H, shifting towards higher frequencies is observed. In the FT-IR spectra, deformation vibrations of the H-O-H bond correspond to the frequency of 1595 cm\(^{-1}\) at the position of the absorption maximum of 1645 cm\(^{-1}\) (figure 3).

The combined presence of absorption of 720 and 1380, 1460, 2852, 2922, 2954 bands indicates the presence of n-hexadecane.

Based on the data obtained, we suggest the following SEO wood impregnation mechanism.

Upon the contact of wood with oil, adsorption occurs, i.e. we can observe the surface intermolecular interaction of wood with motor oil caused by the excess free energy as it is compared to volume. This can be referred to as the result of uncompensated chemical bonds and the desire of the system to minimize its free energy.
The next step is moistening, which is associated with adsorption. Adsorption improves the moistening of the surface by the liquid, which causes predominant adsorption. Thus, the change in surface moistening is a direct consequence of adsorption.

Diffusion in the volume of wood is characterized by the highest activation energy and a low diffusion ratio in comparison with surface diffusion. With an increase in the temperature of the impregnating material to 120°C, diffusion tends to intensify, since within the ‘SEO-wood macrosystem’, the equilibrium shifts towards the endothermic process of oil diffusion into wood, in accordance with Le Chatelier principle. This is confirmed by the thermodynamic justification of more intense penetration of SEO molecules into wood based on a qualitative analysis of the change described by Gibbs’ free energy with increasing temperature of the impregnating solution. Therefore, with a significant increase in temperature (120°C), entropy increases as a result of molecules destruction, the bonds between molecules and in the molecule itself. The number of particles in the composition increases alongside with their degree of freedom. As temperature increases the enthalpy acquires more negative value. Therefore, based on the equation the value of Gibbs’ free energy should have a more negative value, and the probability of diffusion of hot solution molecules into the wood increases as well. As the same mixture is introduced into the hot impregnating solution (based on the average room temperature), the diffusion ratio of SEO molecules decreases, whereas the possibility of the formation of intermolecular bonds increases. Moreover, bonds that retain oxygen in the solution are broken in a hot SEO mixture. The experiment proved that molecular oxygen leaves the solution. Free additional bonds are formed for the interaction of the functional groups of SEO with the respective functional groups of wood. In addition, in our previous work [15], we determined that during high temperature operational mode (180ºC), the size of the molecules decreases from 490 nm for mineral motor oil to 35 nm for mineral motor oil, which is the reason for the better impregnation ability of mineral motor oil of birch wood. Water absorption data for natural wood and wood impregnated with spent engine oil are illustrated in figure 4.

\[
\begin{align*}
\text{y} &= 1.051x + 18.198 \\
\text{R}^2 &= 0.8793 \\
\text{y} &= 0.9137x + 5.3646 \\
\text{R}^2 &= 0.9922
\end{align*}
\]

**Figure 4.** Moisture absorption of natural wood and wood soaked in SEO.

The amount of impregnating composition absorbed by birch wood is 48.8%. Natural wood absorbs 17.96% of moisture in 24 hours. As natural wood remains in a desiccator for up to 720 hours we can
observe the 25.31% increase of water absorption. This process is described by the following equation (2):

\[ y = 1.051x + 18.198 \]  
(2)

This wood absorbs moisture 3 times less than natural wood after 24 hours in a desiccator. Within 720 hours of soaked wood in distilled desiccator water, the moisture absorption value changes in accordance with equation (3):

\[ y = 0.9137x + 5.3646 \]  
(3)

where the amount of water absorbed is twice as less, than it is normally absorbed by the natural wood.

4. Conclusion
The SEO wood impregnation process is based on the intermolecular interaction of the main components of wood (cellulose and lignin) with hydrocarbons and SEO oxidation products (oxidation of paraffin hydrocarbons to compounds with more reactive functional groups such as peroxide, aldehyde and ketone). Therefore, the formation of a hydrogen bond between the functional groups of cellulose (hydroxyl) and lignin (methoxyl, hydroxyl - phenolic and alcohol, carbonyl - aldehyde and ketone, carboxyl, and alkene-type double bonds) and hydrocarbon functional groups and their oxidation products is facilitated. Motor oils are designed for harsh conditions and high temperatures (up to 180°C). Such conditions may cause the destruction of hydrocarbon molecules, their further oxidation and formation of small molecules, which, in its turn, leads to the higher level of penetration of SEO into the wood structure, accompanied by the formation of chemical bonds between the functional groups of the matrix and the filler. This leads to the creation of the new composite material with higher moisture absorption.

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