About the possibility of using 1-vinylnapthalene to modify natural wood

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Abstract. The work studies the possibility of using 1-vinylnapthalene for modification and protective treatment of birch wood. 1-vinylnapthalene used in the work was obtained by the method given in the literature. In order to facilitate the introduction of 1-vinylnapthalene into the wood cavity, hydrocarbon impregnating solutions were prepared on its basis using toluene as a solvent. The samples of birch wood were kept in solutions for 24 hours at a temperature of 20 °C after removing the wood samples from the impregnation baths, toluene was removed using a vacuum. After extracting the bulk of the toluene, the samples were subjected to heat treatment. It is shown that during heat treatment in conducting elements of birch wood under the influence of high temperatures, polymerization of 1-vinylnapthalene proceeds by a radical mechanism. To determine the effect of 1-vinylnapthalene content in wood on the properties of the resulting composites, toluene solutions with different modifier content were prepared. It is shown that with an increase in the content of the proposed modifier in birch wood, water absorption and swelling of samples of the resulting wood-polymer composites significantly decreases, which will increase the service life of products based on modified wood.

1. Introduction
The Russian Federation is one of the owners of the largest territories occupied by forests with a variety of deciduous and coniferous trees. However, rapid urbanization of the territory reduces the area of woodlands. This leads to a decrease in the volume of photosynthesis, oxygen production and makes you think about the future existence of forests on the planet. Integrated and rational use of wood is an important economic and environmental task. And a significant contribution to the conservation of forests is the extension of the service life of wood products.

Wood is a multi-component natural polymer composite. Humanity has been using wood for thousands of years for many purposes: as fuel, construction materials, for the manufacture of furniture, paper and other purposes [1, 2]. This is due to the fact that wood is a unique renewable natural raw material due to the process of photosynthesis.
The role of natural wood as a source of target product is currently continuously increasing, also because the reserves of traditional raw materials of the chemical industry—coal, oil and gas are gradually decreasing. This determines the prospects for its multi-use, as well as research in the field of chemistry and chemical technology of wood.

In addition to the undeniable advantages: high relative and specific strength, elasticity, good thermal insulation properties, human safety and environmental friendliness, wood has a number of disadvantages: the difference in mechanical properties depending on the breed, the susceptibility to changes in shape and size as a result of swelling, shrinkage, warping, the presence of defects and others.

It is possible to reduce or even completely eliminate the above disadvantages by modifying the wood. Modified wood acquires a number of new properties—increased strength, water and moisture resistance, resistance to biological destruction, etc. in comparison with untreated wood. This is achieved by introducing chemically active substances into it. The special attention should be paid to those modifiers that are capable of active chemical interaction with wood components when processing the resulting composites at elevated temperatures. This reduces the leachability of the modifier from the resulting wood composite and increases the service life of the resulting products.

In the literature [1, 3, 4] it is proposed to use oligomeric products obtained from waste and by-products of petrochemistry, urea, phenol - and urea-formaldehyde resins, etc. in order to increase the service life of wood products and increase its physical and mechanical parameters.

One of the ways to modify wood composites is to use polymers ‘in situ’ [5]. For these purposes, radiation polymerization of vinyl monomers in wood materials is used under the action of y-gamma radiation. The polymerization was performed at low temperatures and was accompanied by binding of the resulting polymers to wood components such as cellulose, hemicellulose and lignin. For modification, such monomers as styrene, Acrylonitrile, acrylamide, vinyl acetate, hydroxyalkylacrylates and its mixtures were used [6, 7]. The wood composites modified in this way had an improved set of properties: a more uniform distribution of components, dimensional stability, increased strength indicators, water resistance, and resistance to aggressive environments.

To improve the performance of the resulting wood-polymer composites, in some cases it is recommended to apply heat treatment [8] of modified wood with monomers using free-radical initiators that cause polymerization of these compounds.

In [9], monomer systems such as hydroxyalkylacrylates, its mixtures with methyl methacrylate and 2-vinyl-4,4-dimethyl-2-oxazoline-5-one are considered for filling wood. Improving the properties of wood composites is associated with the mutual blocking of hydrophilic centers in the composition of wood and polymer during the formation of hydrogen bonds. This is also facilitated by reactions within and intermolecular esterification involving hydroxyl groups of monomer and cellulose to form three dimensional structures.

In [10], two types of polymer waste were used to obtain impregnating compounds for modifying products containing wood components: petrochemicals by products and Styrofoam waste due to its joint destruction. The wood-polymer composites based on wood raw materials obtained using this technology had lower water absorption and swelling rates, as well as higher strength characteristics.

Modification of natural wood with siloxane-based compounds [11-12] allows not only to effectively protect wood from adverse factors, but also is environmentally safe.

Good results are obtained by using [13] the used motor oils in compositions containing wood flour for impregnation and modification of deciduous and coniferous wood. This reduces the water and moisture absorption of wood, reduces its swelling in both radial and tangential directions, and also allows you to dispose of production waste.

At the same time, there is no information in the literature on the use of naphthalene derivatives for wood modification, and in particular 1-vinylnaphthalene.

What is the basis for the interest in the use of 1-vinylnaphthalene for wood modification?

This is due to the fact that naphthalene and its derivatives are not deficient and are widely used in various industrial sectors, for the production of dyes and explosives, in medicine, as insecticides, etc.
In industry, naphthalene is obtained from coal tar. At the same time, naphthalene and its derivatives are easily washed out by solvents from products, and volatilize at elevated temperatures. All this reduces the effectiveness of its action. Of interest is the vinyl derivative of naphthalene. Vinyl naphthalene polymers have a fairly high mechanical strength and heat resistance, which can be used in its application to modify and improve the properties of softwood.

The most significant disadvantage of wood is its low ability to resist adverse factors and destructive agents. During atmospheric drying, storage and transportation of timber, wood may be damaged by wood-colouring and mold fungi, which leads to loss of marketability. Protect wood and wooden structures from premature destruction can be some chemical products that are simultaneously poisonous to both fungi and harmful insects. Such chemical products with high antiseptic properties include 1-vinyl naphthalene.

The purpose of this work is to determine the effectiveness of using 1-vinyl naphthalene as a modifier to reduce water absorption and swelling of natural wood.

2. Methods and materials
A number of different methods for obtaining 1-vinyl naphthalene are presented in the literature. For this study, 1-vinyl naphthalene was obtained using a well-known method described in [15]. 1-vinyl naphthalene is a yellowish viscous oily liquid with a density of 1.031 g/cm³. The boiling point of 1-vinyl naphthalene is 270.9°C at 760 mm Hg, the refractive index is 1.653.

In order to effectively carry out the wood impregnation process, it is necessary that the impregnation composition used has sufficient viability and has a low viscosity. The high viscosity of 1-vinyl naphthalene creates great difficulties for the process of introducing it into the wood material. The use of high temperatures for impregnation of wood with 1-vinyl naphthalene is undesirable, since it has an increased polymerization ability and will pass from a liquid to a solid state (in polyvinyl naphthalene) even before penetration into the wood. Taking into account the above arguments for impregnating wood with 1-vinyl naphthalene, it is advisable to prepare hydrocarbon impregnating solutions on its basis. To determine the effect of the content of 1-vinyl naphthalene in birch wood on the properties of the resulting composites, toluene-based solutions were prepared with different content of the modifier used (10, 30 and 50%).

2.1. Conducting the impregnation process
For impregnation, samples of birch wood were prepared with a size of 20 x 20 mm in the radial and tangential directions, with a height along the fibers of 10 mm. Birch wood has a low cost and is the most common wood species in the European part of Russia and Siberia. Samples of birch wood were kept in solutions for 24 hours at a temperature of 20°C. After extraction from the impregnation baths, the samples were placed in a hermetically sealed vessel and under slight heating (40-50°C) under vacuum (100-150 mm Hg), created by a water jet pump, the bulk of toluene was removed through a low-temperature catcher. The decontaminated samples were removed from the vessel and placed in a drying box, where they were kept at a temperature of 160-165°C for 5 hours. During this time, polymerization of 1-vinyl naphthalene and removal of toluene residues took place. After heat treatment, the impregnated samples of birch wood were removed from the drying Cabinet and the resulting wood-polymer composite was placed in the desiccator for cooling. After cooling, the samples were kept for another day at room temperature. The content of the modifier in wood was determined gravimetrically by changing the weight of samples before and after impregnation.

For the obtained modified samples of birch wood, such indicators as water absorption, swelling in the radial and tangential directions.

2.2. Water absorption by wood measurement
To determine water absorption, wood specimens were dried at 105°C in weighing glasses until constant weight, placed in a desiccator under the porcelain grate and covered with distilled water.
After two hours, one, ten and thirty days specimens were weighed. The amount of absorbed moisture was calculated by the formula (1):

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

Whereas: \( m_n \) is the weight of the test tube containing samples, g; \( m_1 \) is the weight of the test tube containing the sample in completely dry state, g; \( m \) is the weight of the test tube, g.

2.3. Swelling of wood determination

Wood swelling was assessed via measurement of their sizes in the tangential and radial directions using calipers with an accuracy of 0.01 mm. Samples used to determine water absorption for two hours, one, ten and thirty days were removed from the desiccant with distilled water and tested for size change.

The values of wood swelling in tangential and radial directions were calculated applying expressions (2) and (3).

\[ a_t = \frac{L_{t_{\text{max}}} - L_{t_{\text{min}}}}{L_{t_{\text{min}}}} \times 100, \% \]  

\[ a_R = \frac{L_{R_{\text{max}}} - L_{R_{\text{min}}}}{L_{R_{\text{min}}}} \times 100, \% \]  

Where: \( L_{t_{\text{max}}} \), \( L_{R_{\text{max}}} \) – size (mm) of samples after water absorption for 1, 10, 30 days in tangential, (\( L_{t_{\text{min}}} \)) and radial (\( L_{R_{\text{min}}} \)) directions, respectively; \( L_{t_{\text{min}}} \), \( L_{R_{\text{min}}} \) – size (mm) of samples in absolutely dry state in tangential and radial directions, respectively.

3. Results and discussion

It should be noted that vinylnaphthalene is well compatible with wood structures. This is due to the fact that 1-vinylnaphthalene has a similar nature to one of the main components of wood – lignin, which consists of a complex of aromatic polymers. Natural lignins contain a variety of functional groups: methoxyl, hydroxyl phenolic and aliphatic, carboxyl, and carbonyl.

1-vinylnaphthalene has a polymerization capacity almost 2000 times higher than styrene. Therefore, during the heat treatment of impregnated wood samples, it will undergo polymerization in the conductive structures of the wood to form polyvinylnaphthalene (figure 1):

\[ n \text{CH}_2=\text{CH} \rightarrow (-\text{CH}_2-\text{CH}^-)_n \]

\[ \text{C}_{10}\text{H}_7 \]

\[ \text{C}_{10}\text{H}_7 \]

Figure 1. Getting polyvinylnaphthalene.

Polyvinylnaphthalene will be less affected by water, aqueous solutions of acid and alkali salts, as well as various organic solvents. The formation of a wood-polymer frame will help to give products not only increased strength indicators, improved water absorption, but also, presumably, to give it antiseptic properties and increase its service life.

The content of 1-vinylnaphthalene, or rather a mixture of 1-vinylnaphthalene and polyvinylnaphthalene (modifier), in the obtained samples, depending on the concentration of the injected solution, varied from 10.3 to 26.8%. The experimental results for determining water absorption and swelling of natural and modified birch wood after 1 and 30 days in distilled water are presented in tables 1 and 2.
Table 1. Effect of 1-vinylnaphthalene content in modified birch wood on water absorption and swelling of samples after 1 day of exposure in distilled water.

| Indicators                                | Natural wood | Content of 1-vinylnaphthalene in modified wood, % |
|-------------------------------------------|--------------|---------------------------------------------------|
|                                           |              | 15.9 | 20.5 | 26.8 |
| Water absorption, %                       | 44.9         | 5.0  | 3.2  | 1.4  |
| Swelling in the radial direction, %       | 5.6          | 4.1  | 3.4  | 2.9  |
| Swelling in the tangential direction, %   | 6.4          | 6.2  | 5.0  | 3.8  |

Table 2. Effect of 1-vinylnaphthalene content in modified birch wood on water absorption and swelling of samples after 30 days of exposure in distilled water.

| Indicators                                | Natural wood | Content of 1-vinylnaphthalene in modified wood, % |
|-------------------------------------------|--------------|---------------------------------------------------|
|                                           |              | 15.9 | 20.5 | 26.8 |
| Water absorption, %                       | 119.2        | 52.4 | 45.5 | 37.2 |
| Swelling in the radial direction, %       | 7.7          | 6.0  | 4.9  | 3.1  |
| Swelling in the tangential direction, %   | 8.3          | 7.5  | 6.2  | 5.5  |

Analysis of the obtained experimental data shows that the higher the modifier content in birch wood, the lower the water absorption and swelling of samples of wood-polymer composites. Thus, 1-vinylnaphthalene can be used for modification and protective treatment of soft low-value wood and production of wood-polymer composites.

To confirm that 1-vinylnaphthalene has increased reactivity, a control test of its polymerization ability at elevated temperatures was performed. The polymerization process of 1-vinylnaphthalene was carried out in a mass at a temperature of 180-185 °C for 5 hours. The resulting polymer was dissolved in toluene and planted in ethyl alcohol. The resulting polyvinylnaphthalene precipitate was separated from the toluene-alcohol mixture and dried in a box at a temperature of 80-85 °C.

Additional introduction of 1-vinylnaphthalene cellulose into the polymerization process in an amount of 5.0% of the total amount of vinylnaphthalene did not have a negative effect on the course of the polymerization process and the polymer yield was 87.7-91.3%.

Thus, control studies have confirmed the above information that 1-vinylnaphthalene will polymerize in the conductive elements of birch wood to form polyvinylnaphthalene.

4. Conclusion
The use of 1-vinylnaphthalene as a modifier of natural wood of low-value soft breeds in combination with high-temperature treatment makes it possible to effectively protect it from adverse factors, reduce water absorption and swelling of wood.

Modified 1-vinylnaphthalene wood can be used in the manufacture of construction parts, finishing materials, furniture.

An approach to polymerization of 1-vinylnaphthalene in conducting elements of birch wood under the influence of high temperatures with the formation of polyvinylnaphthalene has been developed.

For the final decision on the prospects of using 1-vinylnaphthalene for the modification of natural wood, it is advisable to conduct extensive research on the properties of the resulting wood-polymer-monomer composites, which will contribute to the conservation of forest resources and their rational use.
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