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# IDENTIFYING PARAMETERS FOR WOOD PROTECTION AGAINST WATER ABSORPTION

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***An issue related to using wood and timber for building structures is to ensure the stability and durability during operation within wide limits. Therefore, the object of research was the inhibition of the process of water absorption of pine and hornbeam wood during a thermal change in its structure. It is proved that in the process of thermal modification of wood, its structure changes, and, accordingly, water absorption. Namely, the maximum increase in mass under the action of water on an untreated sample of wood was more than 40 %, after thermal modification – less than 35 %. The increase in the mass of wood samples thermally modified and treated with a hydrophobic agent was less than 25 %. On the basis of the obtained results of physicochemical studies, discrepancies were found in the IR spectra of wood, both during thermal modification and with additional treatment with a hydrophobic agent, indicating structural changes in the components. In particular, the decrease or absence of the intensities of the absorption bands of some functional groups and the appearance or intensification of others. On the original hornbeam and pine thermogram, thermally modified, and thermally modified with the addition of a hydrophobic coating, thermogravimetric curves are similar to each other and are characterized by a loss of sample mass. This is possible with increasing temperature due to the processes of dehydration, destruction of hemicellulose, lignin, and cellulose with the formation of a non-combustible residue. During heat treatment of cellulose in the region of temperatures of 150÷450 °C, two processes take place in parallel. This is dehydration, accompanied by the destruction of the pyranose cycle and carbonization to form a carbon residue. Also, the process of destruction of glycosidic bonds while maintaining hydroxyl groups, accompanied by regrouping of pyranose cycles***

***Keywords: thermally modified wood, resistance to water, change in the structure of wood, treatment with a hydrophobic agent***

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## 1. Introduction

Due to its mechanical and operational properties and ease of processing, wood is widely used in construction and architecture. However, it has a number of negative defects, in particular, anisotropy, increased hygroscopicity, which leads to uneven swelling, curvature, and cracking, and bio-damage to wood products during operation, which predetermines the

need for additional processing. Protective treatment helps reduce the sensitivity of wood to moisture and biological damage and expands the scope of use of building structures made of wood.

One of the methods of wood modification is heat treatment, which causes some chemical changes in the structures of the components of the cell wall (lignin, cellulose, and hemicellulose) of wood in order to increase its durability. But thermally modified wood erodes and deteriorates over time. And able to absorb water, which requires additional protection. The application of effective hydrophobic agents requires fundamental research to determine the resistance of products to operating conditions. During the operation of wood under conditions of temperature and humidity fluctuations, individual protective agents dissolve in water and degrade from the surface of the wood. In addition, the lack of theoretical ideas about changes in the structure of wood during thermal modification and the impact on the stability of thermally modified wood hydrophobic agents limit the scale of use of these materials for building structures.

Therefore, studies aimed at determining the properties of wood and changing its structure during thermal modification, which are necessary to determine the parameters of wood protection before water absorption, are relevant.

## 2. Literature review and problem statement

Work [1] notes that the first studies of heat treatment investigated mainly equilibrium humidity, dimensional stability, durability, and mechanical properties. Weight loss, wettability, wood color, and chemical transformations have subsequently been extensively studied, while recent work has focused on quality control, modeling, and studying the causes of improvements. But issues related to the establishment of a change in structure during the modification of wood, modeling and studying the causes of changes in the properties of modified wood remain unresolved.

Study [2] focuses on the analysis of the use of thermally modified wood, which is becoming one of the preferred materials for cladding. Despite the fact that thermally modified wood facades have been in use for more than two decades, there were few reports on long-term monitoring. The results of a three-year monitoring of the thermally modified wood façade in Ljubljana have been published. Moisture content measurement of thermally modified facades was carried out in 22 places and compared to the moisture content of untreated spruce wood. The results confirm the lower moisture content in thermally modified wood compared to reference spruce. However, the moisture content in the wooden façade can be best correlated with the average relative humidity and temperature 48 hours before measuring the moisture content of the wood.

The purpose of study [3] was to determine whether moisture fluctuations are associated with the formation of cracks or roughness. Samples of common spruce, thermally modified spruce, European thermally modified spruce, and European larch core were subjected to artificial accelerated weathering and natural weathering for 9, 18, and 27 months. Then the roughness of the samples was determined using a confocal laser scanning microscope on the axial and longitudinal surfaces at 10× and 50× magnification. After weathering, roughness increased on both axial and longitudinal surfaces. This was evident from profile 2D measurements and surface 3D measurements. The effect of natural weathering on roughness was higher than that of artificially accelerated weathering. Probably due to the synergistic influence of abiotic and biotic factors. This may be due to Wenzel's theory of the effect of roughness on the contact angles of water on the surface. Namely, increased roughness will reduce the contact angle on hydrophilic surfaces. However, it is not specified what methods should be used to improve the properties of modified wood during industrial production.

Paper [4] studied the change in swelling and roughness of the surface of alder wood (*Alnus glutinosa (L.) Gaertn. ssp. glutinosa*) and white elm (*Ulmus glabra Huds.*) after heat treatment at two different temperatures and durations. The modification temperatures were 180 and 200 °C, and the duration was 2 and 4 hours. To assess the surface characteristics of the samples, the stylus method was used. Roughness measurements with a probe were carried out in a direction perpendicular to the fiber on the surface of the wood. Four main roughness parameters were used to assess the effect of heat treatment on the surface characteristics of samples – arithmetic mean deviation of the profile ($R_a$), average height from apex to depression ($R_z$), RMS roughness ($R_q$), and maximum roughness ($R_y$). All parameters of swelling and surface roughness differed significantly for both temperatures and two durations of heat treatment. The established indicators decreased with increasing temperature and duration of processing. But the reactions that occur due to the presence of moisture are not determined.

The purpose of study [5] is to assess the change in color and reflectivity of wooden surfaces due to artificial weathering. The tests were carried out using a solar box chamber that simulates external conditions and subsequent leaching with water. As the weathering time increases, the surfaces of the raw samples darken while the treated samples become lighter. The tendency is to maintain the similarity of color that was at the beginning of weathering tests, or to reduce the chromatic difference. The measured electrical conductivity values are higher in water after leaching of untreated samples and tend to decrease after the first cycles. pH values range from 4.00 to 4.52 in raw and processed samples. FTIR spectroscopy showed that leaching with water caused the loss of materials from samples, mainly from thermally treated ones. FTIR spectra exhibit signatures of polysaccharide materials as the main compounds. Bands of lignin and extractives are also visible. Water leaching seems to remove damaged surface microparticles of wood; but which – not defined.

Thermally modified wood is becoming an increasingly popular material for various applications in buildings [6]. Laboratory studies have shown a positive effect of thermal modification on the durability, dimensional stability, and thermal conductivity of wood. Thus, windows and fa ade elements made of thermally modified European spruce and not modified were tested in the field. Then they were installed on various test sites that have been exposed in different places in Europe (Slovenia, Germany, Sweden, and Spain). The monitoring results showed that elements and windows made of thermally modified spruce have a significantly lower moisture content in the wood compared to those made of unmodified spruce. Applying wax to the surface also had a positive effect on moisture levels. The discoloration of thermally modified wood was more intense compared to unmodified spruce, but successfully slowed down by the addition of pigments to wax. The increase in the amount of mold and stains depended heavily on location, rainfall, and relative humidity.

But issues related to the ability to retain color or reduce the chromatic difference remained unresolved.

In [7], the study of the potential of hyperspectral imaging in the monitoring of commercial consolidating products applied to wood samples was reported. Poplar (*Populus spp.*) and walnut (*Juglans Regia L.*) were chosen to accept a consolidator. Both traditional and innovative products based on acrylic, epoxy and aliphatic compounds were selected. Wood samples were subjected to freezing/thawing cycles to cause material degradation without losing wood components. Then the consolidant was applied under vacuum. Finally, the samples were artificially aged for 168 hours in a solar chamber. The samples were processed in the shortwave infrared range (1000 to 2500 nm) using the SISUChema XL™ device (Specim, Finland) after 168 hours of irradiation. For comparison, color measurement was also used as an economical, simple and non-invasive method to assess the spoilage and effect of wood consolidation. All data were then processed using a chemometric approach completed to determine correlation models based on hyperspectral imaging between materials, wood species, and short-term aging effects. But how thermally modified wood behaves and its stability during artificial aging is not determined.

The purpose of study [8] was to investigate whether the properties of thermally modified wood improve after treatment with oils. Thus, European aspen and fluffy-fluffy birch wood was impregnated with three different oils: water-mixing commercial Elit Träskydd (Beckers oil with propiconazole and 3-iodo-2-propinyl butyl carbamate IPBC), pine resin, and 100 % tung oil. The studied properties of wood impregnated with oils were water-repellent ability, dimensional stability, and susceptibility to mold. Treated wood, especially with pine resin and tung oil, showed an increase in water-repellent properties and dimensional stability. However, Beckers oil, which contains biocides such as propiconazole and IPBC, has shown better protection against mold compared to pine resin and tung oil. Therefore, to increase the stability of wood size, pine resin and tung oil can be used. But treatment with such substances did not significantly improve resistance to mold, and sometimes increased mold growth, while a significant effect against mold was observed on samples treated with Beckers oil.

Study [9] shows the effectiveness of above-ground tests of wood impregnated with epoxidized linseed oil and organofunctional alkoxysilanes. The authors compared achieved results with much more severe underground exposure and initial laboratory tests. Since epoxidized linseed oil and siloxanes are not active ingredients, they have been combined with fungicides for better efficacy. A variety of oils and alkoxysilane retentions and combinations with boric acid, organic fungicides and creosote have been used to impregnate wood and tested. The reference was untreated, treated with chromium-copper arsenate and thermally modified samples. Long-term above-ground and underground testing of the studied compositions led to the conclusion that epoxidized linseed oil in combination with biocides is a suitable protective composition for wood in both above-ground and terrestrial effects. Two alkoxysilanes were more effective for wood exploited above ground. No decay was recorded in epoxidized linseed oil and alkoxysilane-treated samples of overlapping compounds, while untreated control samples were close to breaking down after five years of exposure. But the question of their resistance to bio destruction remains unresolved.

The aim of study [10] was to develop, optimize, and characterize photopolymerizing nano systems based on siloxane modified by the target wing. Specially designed for the preservation and protection of cultural heritage materials (wood, natural stone, etc.). A methacrylate-based resin that hardens under the action of ultraviolet radiation was chosen because it is characterized by high reactivity even at room temperature compared to commercial thermosetting products thermally polymerized in place. Experimental mixtures have been investigated in both liquid and solid states. The dimensions of nanoparticles in liquid compositions solidifying under the action of ultraviolet radiation were first estimated using the analysis of dynamic light scattering. Photocalorimetric analysis was used to analyze the mechanisms of the radical photopolymerization reaction induced by ultraviolet light. The viscosity of the obtained compositions was analyzed using a plate and a plate rheometer as a function of the shear velocity. The compositions were photographically set on a glass substrate using a medium-pressure mercury ultraviolet lamp to measure the following properties – transparency, scratch hardness, and surface hardness, glass transition temperature, and contact angle with water. However, the durability of such a coating is not determined.

Studies [11] of the drying behavior of linseed oil, tung oil, and their 1:1 mixture showed clear differences in wetting when measuring the angle of contact with water of coatings applied to beech and oak wood. Tung oil gave hydrophobicity to all wood samples immediately after application, even without the use of a dryer. Linseed oil required a longer drying time and was more susceptible to substrate exposure but ultimately reached the highest contact angles after forced drying. However, the conditions for inhibition of water absorption are not defined.

In [12], a technique is given that involves covering spruce wood with emulsions without surfactants based on tung oil, linseed oil, or long-oil alkyd resin based on linseed oil. The $\zeta$ potential of emulsions was determined by electrophoretic measurements of mobility. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (ACM) and spectrophotometry were used to study the covered surfaces. Measurements of X-ray photoelectron spectroscopy confirmed the presence of tung oil coatings. Tung oil emulsions were effective at low concentration levels such as 0.04 wt. % of oil content, which is approximately equivalent to 0.04 g $m^{-2}$. And they led to static angles of contact with water, reaching >130°. Measurements of images of scanning electron microscopy and atomic force microscopy provide evidence that the micro- and nanostructures inherent in wood enhance the effect of hydrophobization of the obtained coatings. Another advantage of the method is the minimal impact of the coating on the color and shine of the surface. Thus, a mass-efficient process that meets several principles of environmental engineering has led to an improvement in water-repellent properties without affecting the appearance of wood by coating. But there remained questions related to the resistance of these coatings to use in external conditions.

Thus, from the literary sources above, it has been established that during the thermal modification of wood there are changes in the structures of the components of the cell wall and its properties. This reduces the level of water absorption, but such wood weathers out over time and absorbs water and needs protection. All this gives grounds for conducting a study to determine parameters that enable the use of such wood.

## 3. The aim and objectives of the study

The aim of our work is to identify the parameters of reducing the water absorption of wood with a change in its structure. This makes it possible to justify the directions of expanding the scope of application of wood products.

To accomplish the aim, the following tasks have been set:

– to conduct a study of the process of water absorption by wood under the influence of changes in its structure during thermal modification;

– to study the structure of wood during its thermal modification and coating with a hydrophobic agent.

## 4. Materials and research methods

### 4. 1. Object and hypothesis of research

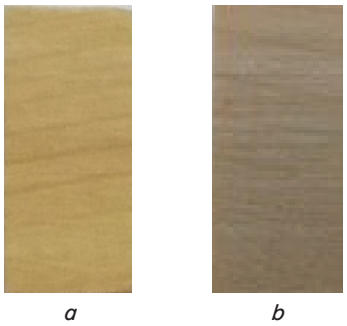
The object of our study is a change in the properties and structure of wood during thermal modification. The scientific hypothesis assumes establishing the inhibition of the degree of water absorption and changes in the structure of wood during thermal modification to justify the conditions for its use.

### 4. 2. Investigated materials and equipment used in the experiment

The studies were carried out using samples of untreated hornbeam and pine wood measuring 20×10×10 mm (Fig. 1).

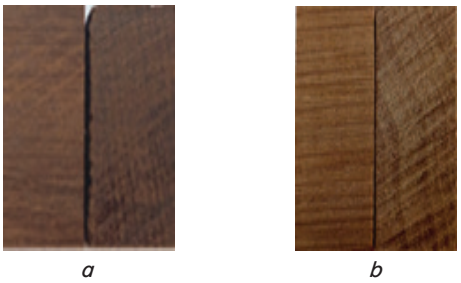
To establish the degree of water absorption by wood, its thermal modification was carried out at a temperature of 220 °C for 10 hours and a hydrophobic coating was applied (Fig. 2). For this purpose, samples of a protective coating of paraffin and rapeseed oil were prepared in the proportion of 90 % oil and 10 % paraffin [13].

Paraffin was dissolved in a steam bath and a certain amount of oil was added and mixed. After cooling to room temperature, it was applied to wood samples with a brush with re-treatment after drying the first layer after 24 hours, with a total consumption of about 148 g/m$^2$ [14].



*a* *b*

Fig. 1. Model sample of wood: *a* – pine; *b* – hornbeam



*a* *b*

Fig. 2. Samples for testing pine and hornbeam wood: *a* – thermally modified; *b* – thermally modified treated with hydrophobic agent

After exposure for 2 days, samples of wood with the resulting protective coating were tested for water absorption.

### 4. 3. Procedure for determining the properties of samples

We determined the amount of water absorption by wood samples according to the working procedure, the essence of which was to experimentally determine the amount of water absorbed by the sample during its exposure in water [15]. To obtain the values of absorbed water by wood, the following equipment was used (Fig. 3).

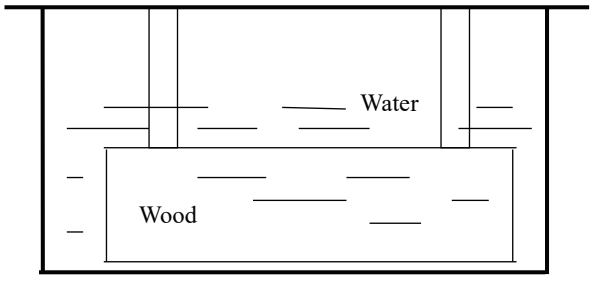



Fig. 3. Cuvette to determine the level of water absorption by wood

The test sample was fixed in a special cuvette so that it was in the water. After a certain period of time, the sample was weighed on the scales and the amount of water absorbed was determined.

Infrared spectroscopy with Fourier transform (FTIR) was performed taking into account [16]. Research method: 0.5 mg of sample crushed from 70 mg of potassium bromide (chipped from a single crystal). From the resulting mixture, the tablet was compressed under a pressure of 10 MPa, achieving maximum optical transparency (to reduce scattering). The spectrum is recorded in the range of 4000–400 cm$^{-1}$, with an optical slit width of 4 cm$^{-1}$, the spectrum was averaged over 12 scans. The analysis was carried out on the Spectrum One (Perkin Elmer) spectrometer (USA).

Thermogravimetric analysis was carried out in accordance with [17]. In order to determine the area of temperatures at which thermal destruction of wood occurs most intensively, thermogravimetric study of destruction processes in a dynamic mode was carried out. Thermogravimetric studies were carried out on the Linseis STA 1400 derivatograph (Germany). Samples weighing 10 mg were heated in an air atmosphere from 20 to 700 °C at a rate of 10 °C/min.

## 5. Identification of patterns of inhibition of water absorption by wood during thermal change of structure

### 5. 1. Investigation of the process of water absorption by wood under the influence of changes in its structure during thermal modification

Reducing the level of water absorption by wood involves its modification, for example, thermal [18], which changes the structure of the wood cell and is able to destroy micro bacteria [19], or its treatment with hydrophobic agents [20].

Table 1 gives the results of water absorption of the sample after exposure to water for 20 days.

Analysis of the results of experiments on water absorption of wood shows that the maximum increase in mass under the action of water on an untreated wood sample was

more than 40 %, after thermal modification – less than 35 %. The increase in the mass of wood samples thermally modified and treated with a hydrophobic agent based on a mixture of oil and paraffin was less than 25 %.

Table 1

The results of the study of the effect of the protective coating on the resistance of wood to water absorption

| Sample | Mass before testing, g | Change in the mass of samples in a humid environment, days | | | | | | | | Amount of water, g |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 0.1 | 1 | 2 | 3 | 6 | 9 | 13 | 20 | |
| Unprocessed pine | 1.54 | 1.91 | 2.20 | 2.35 | 2.38 | 2.43 | 2.62 | 2.64 | 2.82 | 1.28 |
| Raw hornbeam | 1.64 | 2.12 | 2.40 | 2.44 | 2.46 | 2.48 | 2.53 | 2.58 | 2.76 | 1.12 |
| TMW(thermomodified wood) pine | 1.62 | 1.74 | 1.94 | 2.10 | 2.55 | 2.36 | 2.42 | 2.49 | 2.49 | 0.87 |
| Hornbeam TMW | 1.63 | 1.77 | 2.13 | 2.25 | 2.28 | 2.37 | 2.46 | 2.48 | 2.48 | 0.85 |
| Pine TMW with coating | 1.73 | 1.73 | 1.84 | 1.96 | 2.02 | 2.15 | 2.23 | 2.30 | 2.31 | 0.58 |
| Hornbeam TMW with coating | 1.83 | 1.83 | 1.89 | 1.98 | 2.02 | 2.09 | 2.16 | 2.26 | 2.28 | 0.45 |

**5. 2. The results of studies of changes in the structure of wood during thermal modification**

Fig. 4, 5 show the IR spectra of the studied wood samples.

Features of the characteristics of the IR spectra of the studied wood samples. In describing the spectra of samples, it should be borne in mind that wood includes certain proportions of lignin, cellulose, and hemicellulose.

Samples of original and modified pine wood (Fig. 4) have similar absorption spectra. The differences between them are the presence and absence in the first (black) and second (red line) of a weak intensity of the absorption area of 800–832 $cm^{-1}$ with a maximum with a wavelength of approximately 800 $cm^{-1}$. A slight decrease in the absorption of individual absorption bands was also recorded. This wavelength characterizes fluctuations in the glucopyranose ring of cellulose associated with CH and $CH_2$ pendulum oscillations.

Therefore, a decrease in the intensity of the absorption band during thermal modification can be an indicator of the beginning of destructive processes in cellulose. Thus, a decrease in the intensity of the absorption band in thermally modified pine is observed at 1650 $cm^{-1}$. The absorption area of 1650–1630 $cm^{-1}$ is referred to as H–O–H deformation oscillations of crystallization water. A decrease in the intensity of the absorption band during thermal modification indicates a dehydration process that takes place during thermal modification.

The IR spectrum of a pine sample (green line) is an imposition of a spectrum of the hydrophobic agent and thermally modified wood.

Samples of hornbeam wood of the original and thermally modified (Fig. 5), as well as the pine samples discussed above, have similar absorption spectra, but with other minor differences. Thus, in a modified sample of hornbeam (red line) in comparison with the sample (black line), there is a weak intensity of the absorption band with the designation of a maximum with a wavelength of 1035 $cm^{-1}$. In the original sample, the maximum is smoothed, and this absorption band manifests itself in the form of an arm.

Absorption bands at 1000, 1015, and 1035 $cm^{-1}$ correlate with valence oscillations of the C–O-bond in the primary alcohol group in different conformations.

The infrared spectrum of wood is not just the sum of the absorption bands of its individual components, but it also contains bands that characterize the bonds that exist between the macromolecules of cellulose, lignin, and hemicellulose.

To determine the individual characteristics of the wood in question, its identification was carried out by thermogravimetric analysis.

Graphic images of thermogravimetric analysis of wood samples are shown in Fig. 6–8.

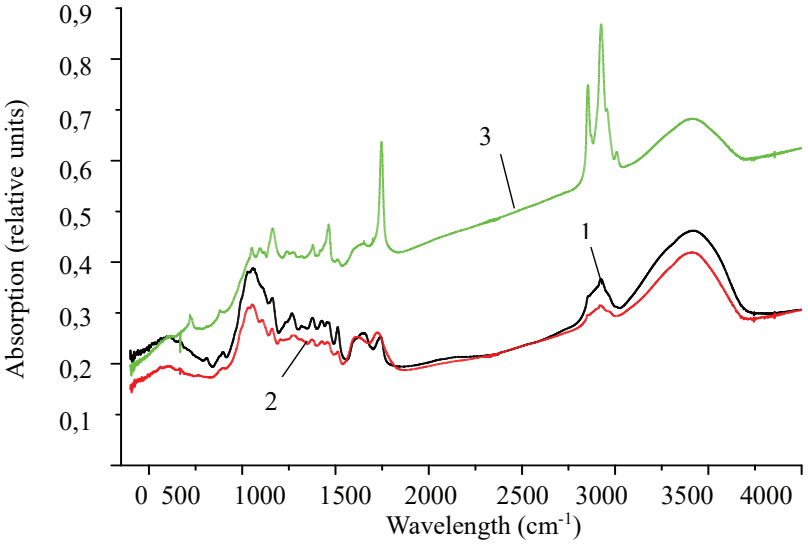



Fig. 4. IR spectra with Fourier conversion of pine samples: 1 – untreated; 2 – thermally modified; 3 – thermally modified and coated with hydrophobic agent

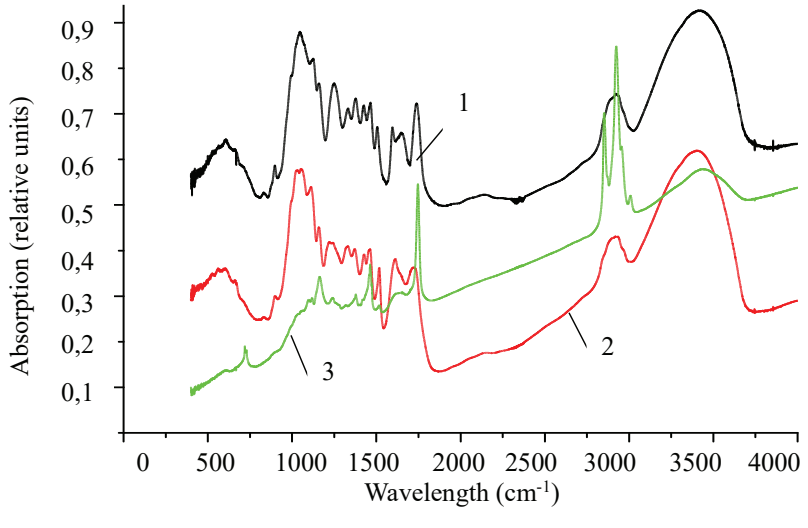
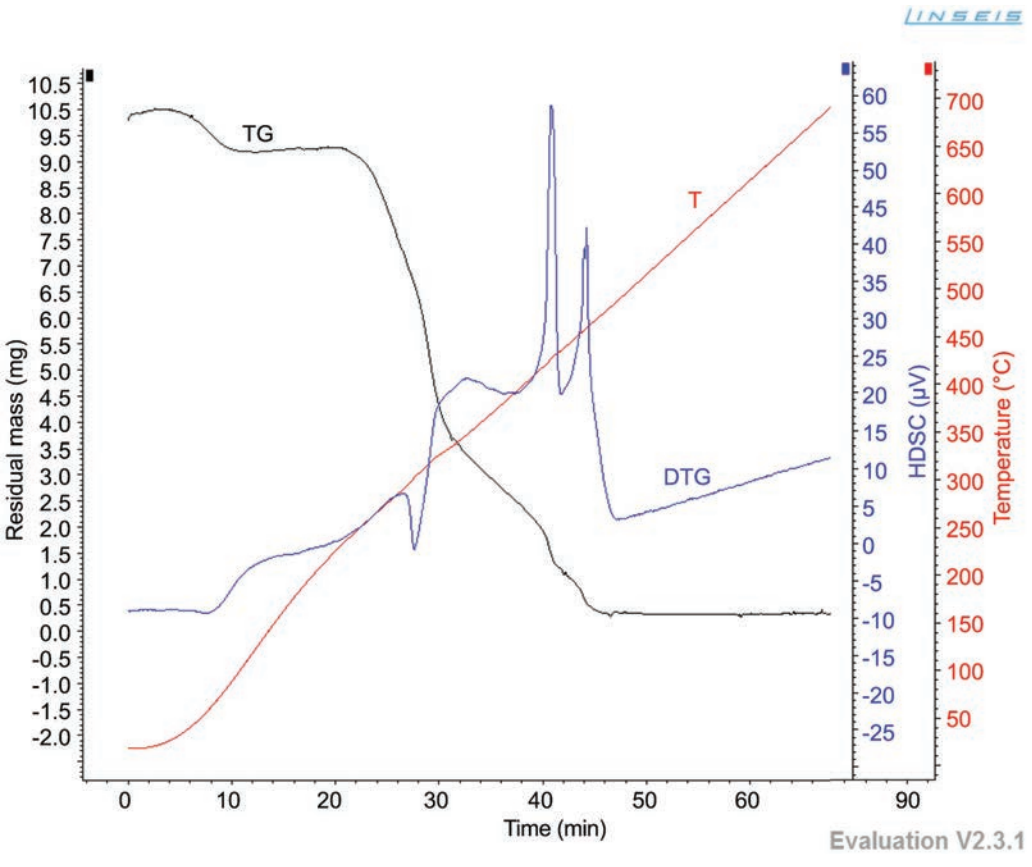



Fig. 5. IR spectra with Fourier conversion of hornbeam sample: 1 – raw; 2 – thermally modified; 3 – thermally modified and coated with hydrophobic agent

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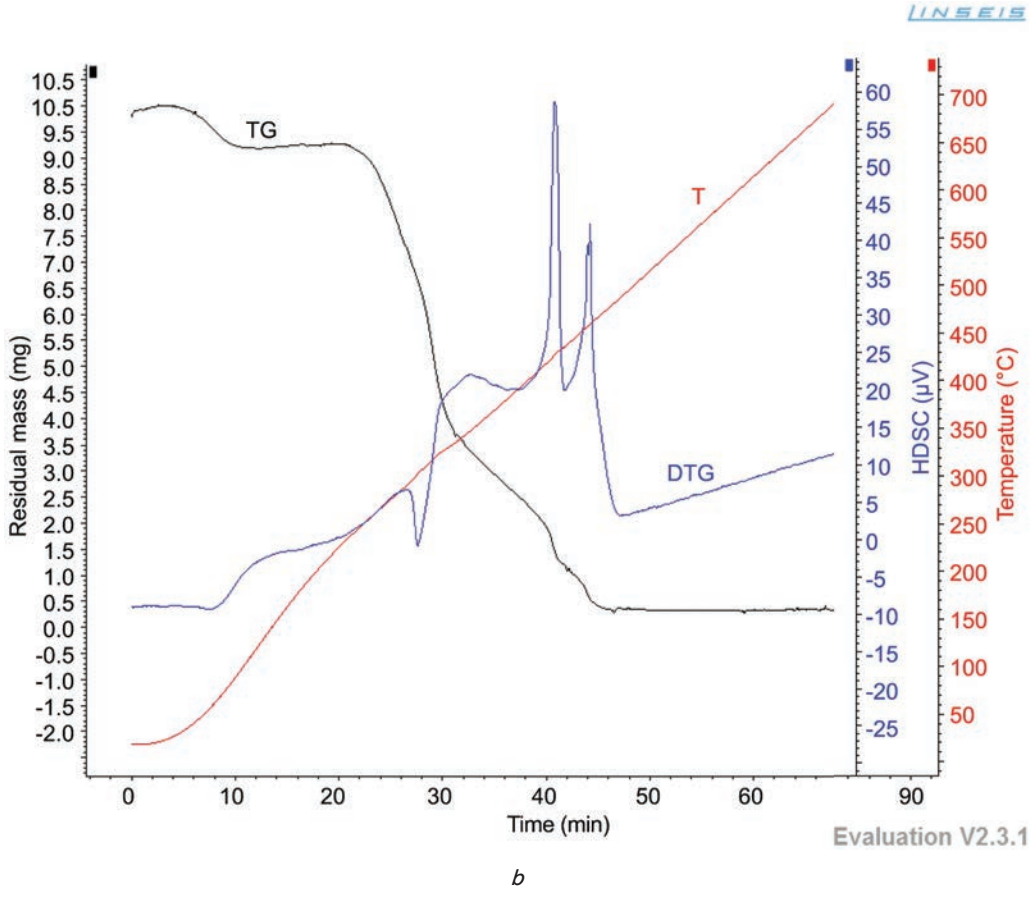
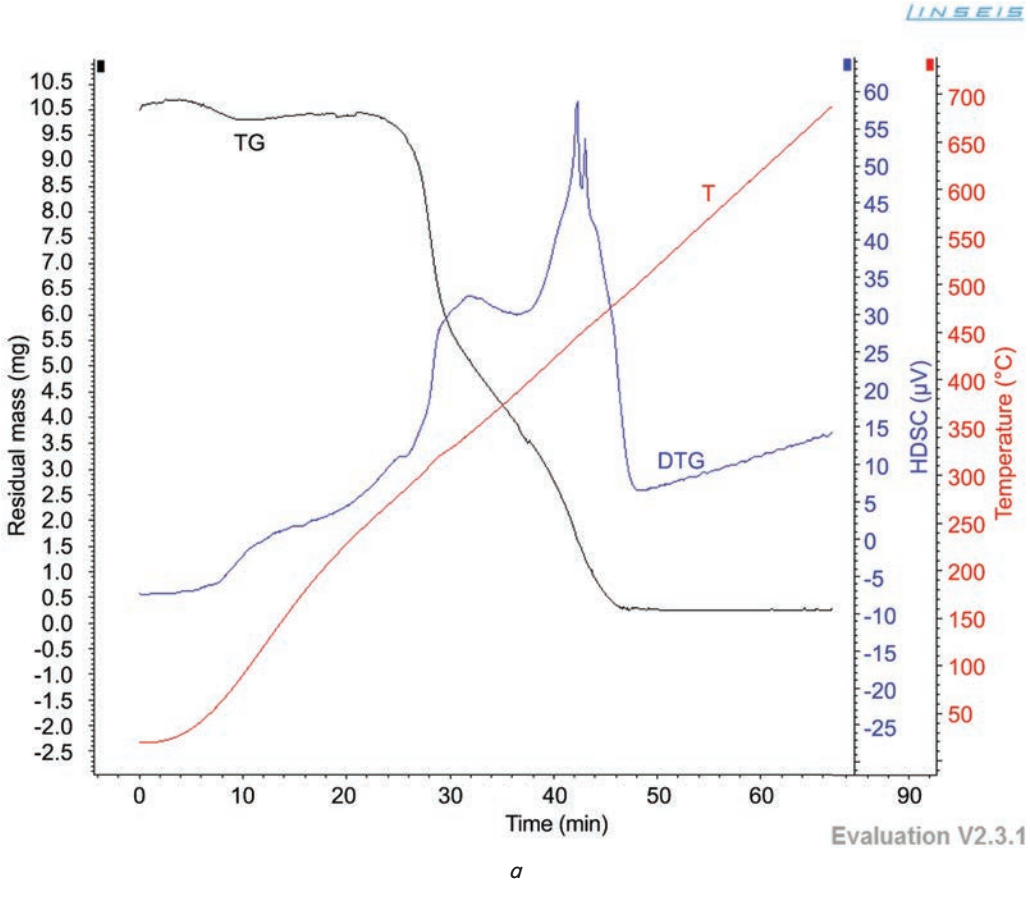



*b*

Fig. 6. Thermogravimetric analysis curves for wood samples: *a* — hornbeam; *b* — pine; T — temperature curve; TG — weight loss curve depending on temperature growth; DTG — differentiated TG curve

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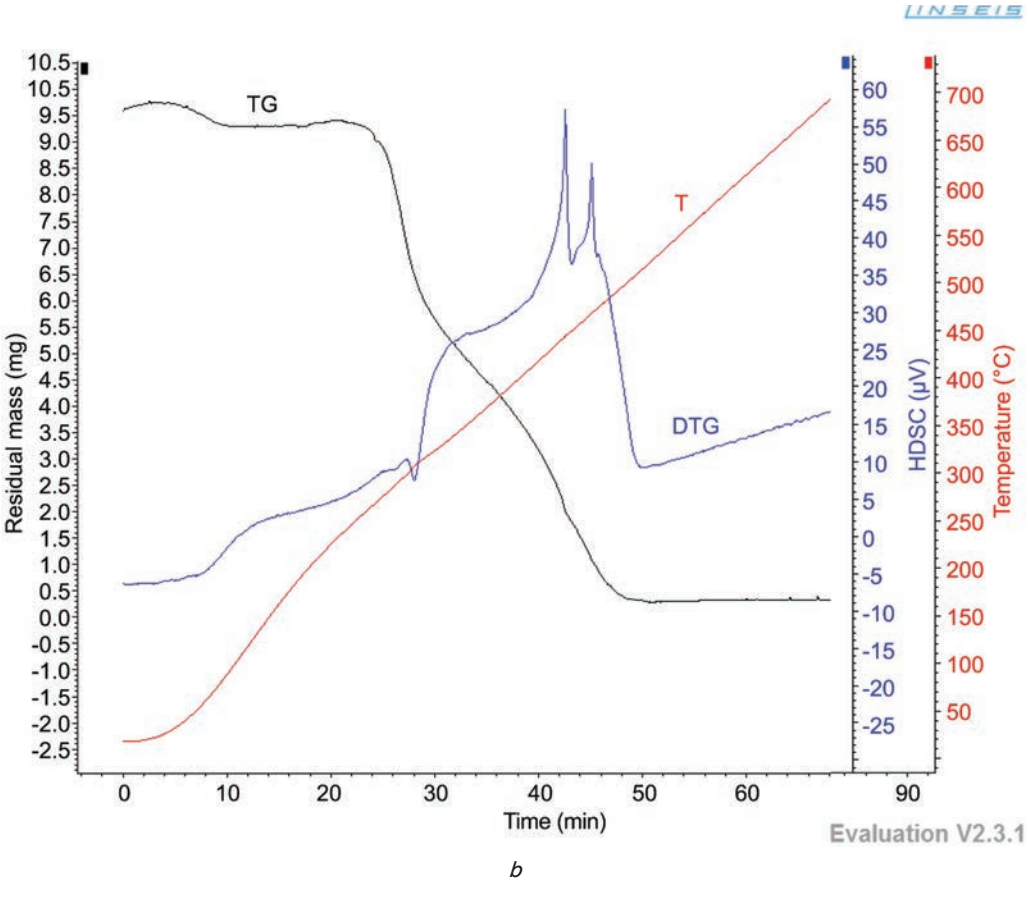
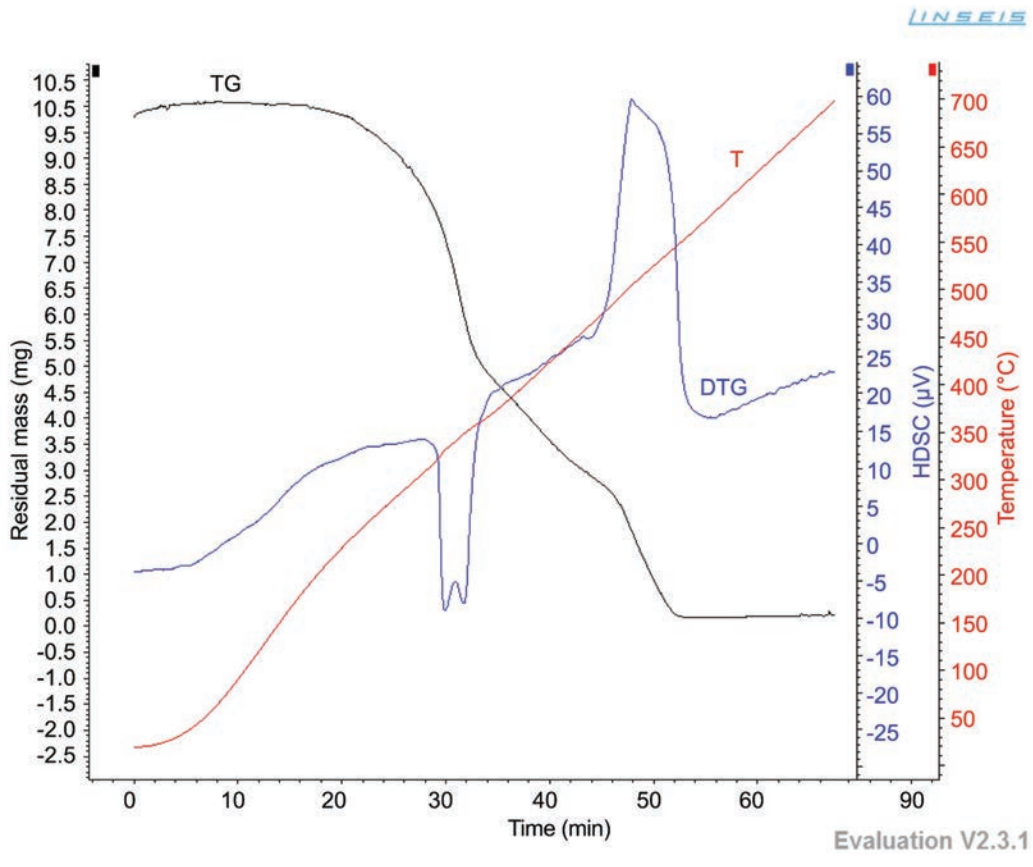



*b*

Fig. 7. Thermogravimetric analysis curves for samples of thermally modified wood: *a* — hornbeam; *b* — pine; T — temperature curve; TG — weight loss curve depending on temperature growth; DTG — differentiated TG curve

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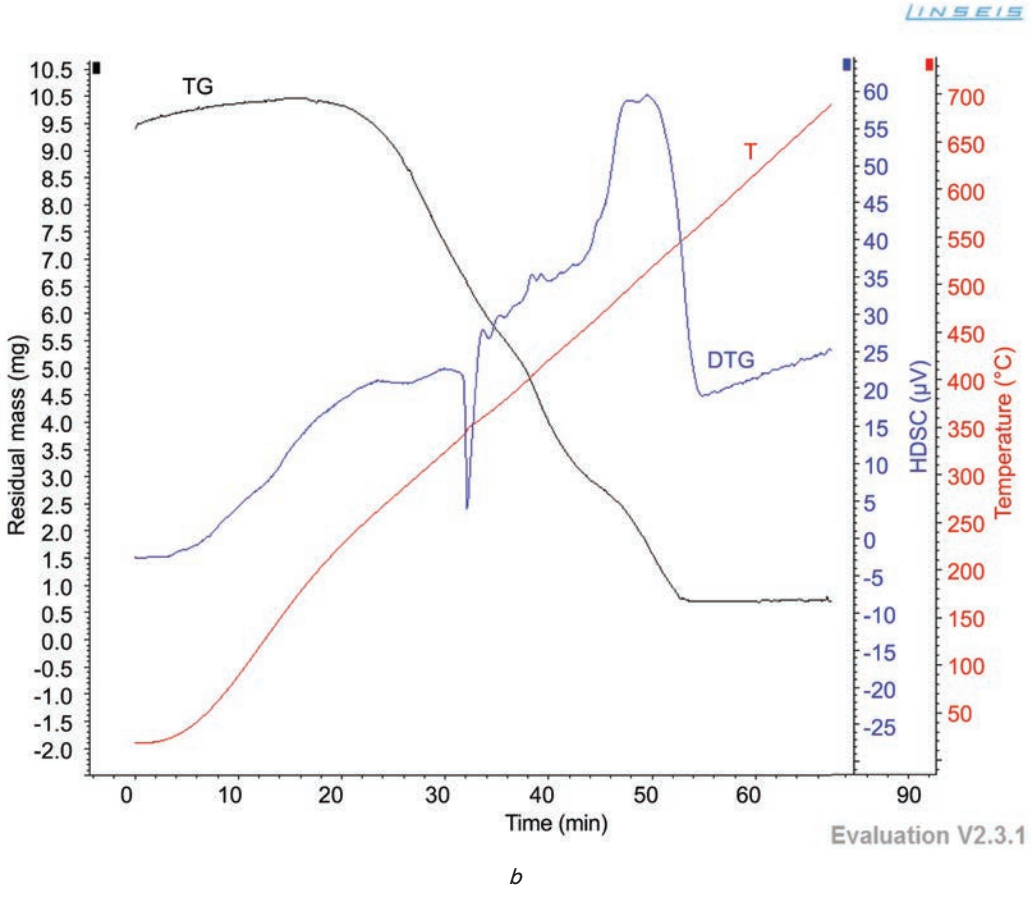


*b*

Fig. 8. Thermogravimetric analysis curves for samples of thermally modified wood with hydrophobic agent: *a* — hornbeam; *b* — pine; T — temperature curve; TG — weight loss curve depending on temperature increase, DTG — differentiated TG curve

On hornbeam thermograms of the original, thermally modified, and thermally modified with the addition of a hydrophobic coating, the TG curves are similar to each other and are characterized by a loss of sample mass with increasing temperature. This is due to the processes of dehydration, destruction of hemicellulose, lignin, and cellulose with the formation of a non-combustible residue. Starting from 40 °C and up to 100 °C, the process of losing free, not bound moisture, by samples takes place. Also, at 40–60 °C, the hydrophobic agent melts. At temperatures of 140–170 °C, lignin decomposes, and, at temperatures in the range of approximately 200–260 °C, hemicelluloses decompose. Cellulose decomposition temperature is 240–350 °C. TG curves after 250 °C show rapid mass loss by samples, which is characteristic of thermal destruction with gas formation and burning of wood. The cessation of mass loss is fixed at 500 °C for the sample of the original hornbeam, at 515 °C – for a sample of hornbeam thermally modified, and at 566 °C – for hornbeam thermally modified with the addition of a hydrophobicizer.

On the DTA curves, a smooth rise is observed from 40 °C to 140 °C and it has the appearance of an arm. Further, too, the curve rises to 280–300 °C (thermal destruction of cellulose).

During the heat treatment of cellulose in the region of temperatures of 150–450 °C, two processes take place in parallel:

– dehydration, accompanied by the destruction of the pyranose cycle and carbonization with the formation of a carbon residue and a complex mixture of volatile products;

– destruction of glycosidic bonds while maintaining hydroxyl groups, which is accompanied by regrouping of pyranose cycles with the predominant formation of a volatile product – levoglucosan.

On the DTA curve, after a smooth rise, an endoeffect is observed with a maximum at 335 °C. For a thermally modified sample, it is weakly expressed, and for thermally modified with a hydrophobic coating one, it is forked. The latter may be explained by the specific blocking of the processes of decomposition, gas emission, or changes directly in the hydrophobic agent.

This endoeffect is associated with the destruction of cellulose and the formation of volatile levoglucosan. For a thermally modified wood sample, the endoeffect is mild due to the reduced formation of levoglucosan due to the already partially restructured cellulose.

After the endothermic peak, heat dissipation increases to 350 °C – the end temperature of cellulose decomposition. After that, there is a sharp rise on the DTA curve with two maxima at 432 and 463 °C for the original hornbeam sample, and 446 °C, 456 °C for a thermally modified wood sample. The first two indicated maxima are the process of flame combustion of decomposed cellulose to form a carbon residue, And the second two highs indicate the burnout of this residue itself. The DTA curve after 350 °C has a different form – after a smooth rise to 450 °C, a sharp rise occurs with a maximum at 500 °C, followed by a decrease in heat generation in the form of an arm. Probably, there is a partial blocking by the hydrophobic agent of air access to burn the carbon residue, and when the decomposition temperature is reached, their joint burnout takes place. For all hornbeam samples after carbon residue burnout, the DTA curve goes down, which indicates complete combustion to a non-combustible residue of inorganic nature.

The same patterns of destruction with weight loss and thermal effects are observed on thermograms of the original pine, thermally modified pine, and thermally modified with a hydrophobic agent, with minor differences. Thus, on the DTA curve of a thermally modified sample of wood with a hydrophobic agent after 350 °C, it is observed with several mild exoeffects and weakly expressed forked maximums of complete burnout of cellulose and carbon residue.

An interesting feature for samples of hornbeam and pine is the following. The endoeffect in question at 335 °C is manifested in the original samples, and for thermally modified – it is mild (especially for hornbeam). Instead, for a thermally modified one with a hydrophobic agent, the endoeffect appears again. The mechanism of action of the hydrophobic agent on thermally modified wood, which resumes the appearance of the endoelectric effect, has not yet been established and requires additional research.

## 6. Discussion of results of the study of changes in the properties of wood during thermal modification

In the study of water absorption by wood after thermal modification and application of a protective coating, as follows from the results obtained (Table 1), the process of inhibition of the time of penetration of water is natural. This is due to a change in the structure of wood during thermal modification (Fig. 4, 5), which is confirmed by the transformation of minor structural changes in cellulose, lignin, and wing by the data obtained by the method of IR spectroscopy with Fourier transform. They are associated with the intramolecular restructuring of the components of wood and changes in intermolecular bonds between them. And an additional formation of a protective shell on the surface of the wood during the polymerization of the hydrophobic agent reduces the processes of water penetration into the wood and its subsequent destruction.

It should be noted that thermal modification of wood leads to chemical transformations of wood components capable of inhibiting the process of water penetration. Obviously, such a mechanism of influence of thermal modification is the factor in regulating the process by which the resistance of wood to water absorption decreases. And the presence of a polymer shell of a hydrophobic agent leads to the formation on the surface of the wood of an elastic film resistant to water penetration. In this sense, there is an interpretation of the results of determining the water absorption of wood, namely the increase in the mass of samples after exposure in water. Thus, the maximum increase in mass in the case of water absorption by an untreated sample of wood was more than 40 %, after thermal modification – less than 35 %. The increase in the mass of wood samples additionally treated with a hydrophobic agent was less than 25 %. This indicates the formation of a barrier for water penetration, which can be identified by direct contact with water.

This means that taking into account the fact of inhibition of the absorbing effect of water with thermally modified wood opens up the possibility for effective regulation of wood properties in industrial production conditions. Analysis of experimental studies on changing the structure of wood during thermal modification and studies on determining the thermogravimetric studies indicates changes in thermal effects. During heat treatment, there are processes of dehydration with the destruction of wood components (Fig. 7).

This does not disagree with the practical data known from works [5, 12], the authors of which, by the way, also

associate a decrease in the water absorption of wood with a change in the structural composition. But, unlike the results of studies reported in [6, 21], the data obtained on the effect of thermal modification on the properties of wood, in particular, on water absorption, suggest the following:

– the main regulator of reducing the water absorption of thermally modified wood is a change in the structure in the components of wood;

– hydrophobization processes (oil-waxes, oils, paraffin) have a significant impact on the process of protecting wood from the effects of water.

Such conclusions may be considered appropriate from a practical point of view since they allow a reasonable approach to both thermal modification and determining the required amount of protective agent. From a theoretical point of view, this suggests determining the mechanism of processes of inhibition of water permeability, which are certain advantages of this study. Therefore, the scope of application of the results of thermal modification of wood will increase its scope.

However, it is impossible not to note that the results of determining the amount of water absorbed (Table 1) indicate the ambiguous effect of changing the structure of wood on thermal decomposition. This is manifested primarily in the increase in the mass of the sample during tests of thermally modified wood with a hydrophobic agent. Therefore, the conditions for applying the results of research are not limited to the use of the above wood species. Such uncertainty imposes certain restrictions on the use of the results obtained, which can be interpreted as the disadvantages of this study. The inability to remove these restrictions in the framework of this study gives rise to a potentially interesting direction for further research. In particular, tests can be focused on identifying the moment in time from which an intensive decrease in the water absorption of wood begins. Although the potentially expected effects of the use are an increase in the resistance of wood to destruction. Such a detection will make it possible to investigate the structural transformations of wood that begin to occur at this time, and to determine the input variables of the process that significantly affect the beginning of such a transformation.

## 7. Conclusions

1. Resistance to water absorption of wood shows that during the thermal modification of wood, its resistance to water increases. Namely, the maximum weight gain in the case of water absorption by an untreated sample of wood was more than 40 %. After thermal modification – less than 35 %, and the increase in the mass of wood samples treated with a hydrophobic agent based on a mixture of oil and paraffin was less than 25 %.

2. Based on the results of physical and chemical studies, the following conclusions can be drawn:

– the revealed discrepancies in the IR spectra of wood, both during thermal modification and with additional treatment with a hydrophobic agent, indicate structural changes in the constituent components – a decrease or absence of the intensity of the absorption bands of some functional groups and the appearance or intensification of others;

– thermogravimetric analysis data indicate complete burnout of thermally modified wood. On thermograms of the hornbeam of the original, thermally modified, and thermally modified with the addition of a hydrophobic coating, thermogravimetric curves are similar to each other and are characterized by a loss of sample mass with increasing temperature. This is due to the processes of dehydration and destruction of hemicellulose, lignin, and cellulose to form a non-combustible residue. During heat treatment of cellulose in temperature regions 150–450 °C two processes take place in parallel. This is dehydration, accompanied by the destruction of the pyranose cycle and carbonization with the formation of a carbon residue and a complex mixture of volatile products. Also, the process of destruction of glycosidic bonds while maintaining hydroxyl groups, accompanied by the rearrangement of pyranose cycles with the predominant formation of a volatile product – levoglucosan. The nature of the burnout of the coke residue in wood samples makes it possible to accept assumptions about the coke residue of different qualitative and quantitative composition, which is formed due to structural changes in wood components.

## Conflicts of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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## Data availability

All data are available in the main text of the manuscript.

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