Physical and mechanical characteristics of a composite material made of birch wood hydrolyzed in the presence of hydrogen peroxide

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Abstract. The results of research of physical and mechanical characteristics of the plate composite material obtained from birch wood after its processing by the method of explosive autohydrolysis are shown. Before barothermal treatment, the wood was impregnated with an aqueous solution of hydrogen peroxide. The composite material is made from hydrolyzed wood pulp by hot pressing without adding binders. It was found that the properties of the composite material depend on the amount of hydrogen peroxide and the rigidity of the barothermal treatment conditions. Each of the modes of barothermal treatment corresponds to a certain value of the amount of hydrogen peroxide, when using which the density of the material reaches the maximum value. The dependence of the bending strength of a composite material obtained using different amounts of hydrogen peroxide is characterized by the presence of an extremum point. At this point, the strength value is the maximum. Further increase in the amount of hydrogen peroxide is accompanied by a deterioration in strength characteristics. It is suggested that the effect is a consequence of the dominance of destructive processes over the processes of intermolecular crosslinking when using a large amount of hydrogen peroxide.

1. Introduction
One of the areas of application of crushed wood is the creation of composite materials for structural purposes on its basis. Obtaining wood composite materials with the specified properties requires the development of predictive models. Based on them, optimal technological modes can be selected.

One of the methods for obtaining composite materials from raw materials of plant origin is based on the use of the method of explosive autohydrolysis. At the first stage, the material is hydrolyzed in an acidic environment of saturated water vapor. On the second – hot pressing into a composite material. Such materials can be obtained without the use of binders [1, 2].

Explosive autohydrolysis is a type of hydrolytic treatment of lignocellulose materials. The method is based on processing plant raw materials in a saturated water vapor environment for a specified time, after which a sharp pressure drop to atmospheric pressure is performed. The processed material is released into the receiving device [1, 3-8]. The result of deep hydrolytic transformations of wood tissue during steam treatment is the appearance of new low-molecular components in its composition and significant changes in the morphological structure. Such processes can have a significant impact...
on the qualitative and quantitative composition of the resulting product and its cost [9]. Recent studies show increased attention to the study of the effects of chemicals (hydrolyzing agents) on the kinetics of hydrolytic processes in explosive autohydrolysis, on the composition and characteristics of the resulting components [10-14]. Such research is mainly carried out in the framework of projects for the development of biofuel technologies. It should be assumed that the use of hydrolyzing agents can contribute to improving the processes of obtaining other substances and materials based on the method of explosive autohydrolysis, including composite materials.

The goal of this work is to study the effect of processing birch wood with hydrogen peroxide on the physical and mechanical characteristics of the composite material obtained from it after barothermal treatment by explosive autohydrolysis. The addition of hydrogen peroxide to wood affects the kinetics of lignin depolymerization and hemicellulose hydrolysis. Processing under such conditions can significantly soften the conditions of explosive autohydrolysis, without compromising the characteristics of the obtained materials [15].

2. Methods and Materials

The process of obtaining the composite material investigated in the presented work is carried out as follows. Air-dry technological birch chips with an average particle size of ~ 5×15×25 mm were used as a feedstock. Pretreatment of wood chips was performed by impregnation with an aqueous solution of hydrogen peroxide taken in an amount of 0..33.0 m. h. / 100 m. h. of wood in terms of "dry" substance H₂O₂. The volume of the solution was always brought up to a ratio of 1/1 to the weight of the original wood. Processing temperature ~ 293K, duration – 60 min.

After water-peroxide treatment, the wood chips were placed in a reactor of a laboratory installation of explosive autohydrolysis of periodic action. In the reactor, it was subjected to barothermal treatment in a saturated water vapor environment at a set temperature for a set time. The processing temperature in the series varied in the range from 443 to 463 K. The processing duration was from 5 to 15 min. The factor of process stiffness calculated by [16] matched to the range R₀ from 575 to 4466 min. After the completion of barothermal treatment, the pressure was reset to atmospheric. The release of hydrolyzed material to the receiving device was carried out in no more than 1 second. The resulting material was dried in a room at room temperature under natural ventilation conditions.

The process of hot pressing the composite material was carried out in a collapsible mold at a temperature of 423K and a pressure of 5MPa. The duration of pressing after reaching the target temperature was ~ 1 min/1 mm of plate material thickness. Pressing was carried out without introducing in the press a lot of binders.

Determination of density, strength in static bending, water absorption and swelling was performed according to standard methods in accordance with the requirements of GOST [17-19].

3. Results and Discussion

The influence of barothermal wood processing conditions in the presence of hydrogen peroxide on the physical and mechanical properties of the resulting plate composite material is determined. Based on the research materials, the dependences of density, bending strength and hydrophobic characteristics for different conditions of barothermal treatment and different amounts of hydrogen peroxide were obtained.

Figures 1–8 show the dependence of the density and strength of the composite material on the amount of hydrogen peroxide added to the wood. It is found that all dependencies are characterized by an initially sharp increase in the density of the composite material with an increase in the amount of the hydrolyzing agent. After reaching a certain density value, no further increase is observed. The discovered effect is a consequence of the intensification of hydrolytic transformations of wood components with an increase in the amount of hydrogen peroxide used. It should be assumed that for each of the conditions of barothermal treatment, the presence of its own threshold value of the amount of H₂O₂ is characteristic, at which the maximum possible degree of dispersion of the hydrolyzed wood
substance is achieved. This results in a composite material with maximum density. Further, the density of the material does not increase.

Figure 1. Dependence of the density and strength of the composite material from the amount of hydrogen peroxide (processing 5 min. at 443K ($R_0=575$ min.)).

Figure 2. Dependence of the density and strength of the composite material from the amount of hydrogen peroxide (processing 5 min. at 453K ($R_0=1133$ min.)).

Figure 3. Dependence of the density and strength of the composite material from the amount of hydrogen peroxide (processing 10 min. at 443K ($R_0=1151$ min.)).

Figure 4. Dependence of the density and strength of the composite material from the amount of hydrogen peroxide (processing 15 min. at 443K ($R_0=1726$ min.)).

Figure 5. Dependence of the density and strength of the composite material from the amount of hydrogen peroxide (processing 5 min. at 463K ($R_0=2233$ min.)).

Figure 6. Dependence of the density and strength of the composite material from the amount of hydrogen peroxide (processing 10 min. at 453K ($R_0=2267$ min.)).
Dependences of strength characteristics have a different character. The strength value is directly proportional to the density only for relatively small amounts of hydrogen peroxide. Under any conditions of barothermal treatment, the bending strength, having reached the maximum value, begins to decrease with a further increase in the amount of H$_2$O$_2$. It is most likely that the detected effect is due to the activation of the processes of destruction of wood components when using large amounts of hydrogen peroxide. In this case, the components responsible for forming chemical bonds in the future composite material are subject to destructive changes. These are products of hydrolysis of hemicellulose and lignin.

The amount of hydrogen peroxide that determines the production of a composite material with the maximum strength value decreases with increasing duration of barothermal treatment or its temperature (figure 9). In the performed series of experiments, the maximum strength at the minimum value of the amount of H$_2$O$_2$ is achieved at the barothermal treatment temperature of 463K for 10 min. ($R_0 = 4466$ min.). A similar effect is achieved at a temperature of 453 K. In this case, the duration of barothermal treatment should be increased to 15 minutes ($R_0 = 3400$ min.).

The maximum value of bending strength is achieved when using hydrogen peroxide, taken in an amount from 5 to 24 m. h. Under barothermal treatment, for example, at a temperature of 443K and a duration of 5..10 minutes ($R_0 = 575..1150$ minutes), the effect of hydrogen peroxide becomes noticeable when its content exceeds 3 m.h. Consequence of a further increase in its content is a sharp intensification of the process of increasing both the density and mechanical strength. Maximum strength indicators are provided with a significantly smaller amount of catalyst used. In General, the dependence of the bending strength on the stiffness factor of explosive autohydrolysis is close to linear (figure 9).

For composite material samples obtained under the conditions of barothermal treatment process rigidity $R_0 = 4466$ min., the dependences of water absorption and swelling in 24 hours were determined. The type of dependencies is shown in figures 10, 11. With an increase in the amount of hydrogen peroxide, there is initially a sharp improvement in hydrophobic characteristics. The reduction of water absorption reaches 50%, and the swelling reaches 30% of the values of these indicators for a composite material obtained without the use of hydrogen peroxide. Both dependencies are inversely exponential. With an increase in the amount of hydrogen peroxide, the dynamics of improving water absorption and swelling differ. If the water absorption depends linearly on the density (figure 12), then the swelling curve is smoother. Thus, the decrease in swelling does not occur synchronously with the increase in the density of the material, and the dependence of swelling on water absorption has a complex nonlinear character (figure 13).
Figure 9. Dependence of the optimal amount of hydrogen peroxide (determined by the maximum bending strength) from the rigidity of barothermal treatment conditions.

Figure 10. Dependence of water absorption of the composite material for 24 hours on the amount of hydrogen peroxide in the solution for impregnation of chips (processing 10 min. at 463K ($R_0=4466$ min.)).
Figure 11. The dependence of the swelling of the composite material for 24 hours on the amount of hydrogen peroxide in the solution for impregnation of chips (processing 10 min. at 463K ($R_0=4466$ min.)).

Figure 12. Dependence of water absorption of a composite material for 24 hours on its density.
4. Conclusion
The application of hydrogen peroxide as a hydrolyzing agent at the stage of barothermal processing of birch wood contributes to the intensification of hydrolytic transformations in its components. Plate composite material obtained from wood hydrolyzed in the presence of hydrogen peroxide has high physical, mechanical and hydrophobic characteristics. Varying the amount of hydrolyzing agent and the conditions of barothermal treatment (duration and temperature) allows you to obtain a composite material in a wide range of properties. The complex action of different amounts of hydrogen peroxide and the temperature-time factor of the barothermal treatment process on birch wood determines the possibility of obtaining a composite material with high performance indicators. The optimal processing parameters should be considered:

- the amount of hydrogen peroxide used in the pre-impregnation stage of wood is 6..9 m. h. per 100 m. h. of raw wood;
- the rigidity factor of the explosive autohydrolysis process is 3400..4466 min.

The used modes allow obtaining a composite material characterized by physical and mechanical parameters in the following ranges:

- density ~ 1100..1350 kg / m$^3$;
- static bending strength ~ 35..55 MPa;
- water absorption in 24 hours ~ 11..Eighteen %;
- swelling in 24 hours ~ 10..18 %.

Based on the presented dependencies, technological modes of obtaining a plate composite material from hydrolyzed birch wood with specified physical and mechanical characteristics can be selected.

The advantage of using hydrogen peroxide as a hydrolyzing agent is due not only to the activation of hydrolytic processes in wood components and the formation of additional amounts of reactive groups in them. Hydrogen peroxide is an unstable substance that is subject to decomposition into oxygen and water. The intensity of decomposition processes increases in the harsh conditions of barothermal wood processing. Thus, the use of this substance, in contrast to mineral acids and other more stable hydrolyzing substances, reduces the likelihood of a destructive effect on the composite material during the operation of products obtained from it.
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