Increase of fire protection and strength of wooden structures by modification in a thin surface layer by nanodispersion composites

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Abstract. Currently, the industrial construction of multi-storey houses of wooden structures (DK) is increasing. In world practice, multi-storey buildings from a recreation center are being built in Austria, Great Britain, Norway, and Canada. In Russia, 9-13 storey buildings are being designed using a recreation center. High-rise construction using a recreation center for earthquake-prone areas is especially relevant. For modern multi-story building from a recreation center, effective surface fire protection should not increase the weight of structures. At the same time, their strength should increase. The solution of complex issues of DC fire protection in thin layers with a simultaneous increase in its strength is an unresolved problem.

1. Introduction

Wood and wood materials are fire hazardous materials. Fire protection of a recreation center is an important component of fire safety [1-5]. For modern multi-story building from a recreation center, effective surface fire protection should not increase the weight of structures. At the same time, their strength should increase. The solution of complex issues of DC fire protection in thin layers with a simultaneous increase in its strength is an unresolved problem [6-8]. An effective way to improve the operational characteristics of wood is a soft adsorption-chemical modification [9]. Soft modification consists in applying a thin (1.0-1.5 mm) layer of the modifier on the surface of the DC at temperatures of 10-30 °C. Under these conditions, the modifiers must have high reactivity to form chemical bonds with the substrate. Effective modifiers should have a set of protective properties - reduce flammability, increase hydrophobicity and biostability.

The burning process of building materials, including wood, is preceded by thermal oxidative degradation. With soft modification, the activation energy of thermal decomposition processes increases.

The most effective flame retardants that reduce the combustibility of wood are phosphorus compounds. For mild modification, phosphorus-containing organic compounds (FOS) are most effective [18-19]. Esters of phosphoric, including phosphonic, acids reduce the combustibility of wood. Moreover, they form chemical bonds with the substrate, for example, with the surface of the DPP. The mechanism of their action is to increase the activation energy of thermal decomposition processes, reduce combustibility, and also to increase hydrophobicity and biostability. As nanoscale surface modifiers, we used carbon nanotubes (CNTs).

2. Methodology

2.1. Comparison of the fire retardant properties of wood when modified with sandwich coatings

Research was conducted on pine sapwood wood samples. Phosphonic acids were used as modifiers: methylphosphonic acid (MF), nitrilotrimethylphosphonic acid (NTP) and carbon nanotubes (CNTs).
The structure of the modified surface and its elemental composition were studied using a dual beam electron microscope Dual Beam. The strength of nanomodified samples was determined according to GOST 16483.26-72. Fire hazard was determined by the needle flame method also in accordance with GOST.

**Table 1.** The effect of dimethylphosphite on the properties of wood with soft surface modification.

| Parameters                        | Native wood | Dimethylphosphite treated wood |
|-----------------------------------|-------------|--------------------------------|
| $E_{act.}$, KJ / mol              | 148,1       | 292,4                          |
| Wetting angle, $\cos \theta$      | 0,56        | 0,67                           |
| Biostability                      | -           | +                              |
| Mass loss on combustion $\Delta m,\%$ | 79,0   | 5,9                            |

The concentration of the FOS modifier is 30%; CNTs were used in the form of aqueous suspensions with a concentration of 0.01%. Aqueous FOS solutions were applied to the surface at a rate of 80 g / m². Aqueous suspensions of CNTs of various concentrations were applied at a rate of 180 g / m². With the surface application of aqueous suspensions of CNTs of various concentrations, the weight loss was 70-56%. Therefore, CNTs do not have flame retardant properties. Surface modification of CNTs does not reduce the fire hazard of structures. With the surface application of FOS modifiers, the weight loss is 8.9-6.2%. We studied the possibility of enhancing flame retardant properties by creating a sandwich coating with the participation of CNTs. Fire-retardant compositions were two-component systems consisting of a protective layer of phosphonic acid and a second layer of nanodispersed CNTs.

![Figure 1. The scheme of the sandwich coating](image)

Coating wood with sandwich compositions transferred wood to the category of slow-burning materials as evidenced by the data from table 2.

**Table 2.** The determination of fire hazard of modified wood by GOST 27484-87.

| No | Composition             | Duration of smoldering $t_{sm}$, sepp. | Weight loss $\Delta m,\%$ |
|----|-------------------------|----------------------------------------|---------------------------|
| 1  | CNT 0.01% + NTF 30%     | 0                                      | 3,37                      |
| 2  | CNT 0.05% + NTF 30%     | 0                                      | 6,03                      |
| 3  | CNT 0.1% + NTF 30%      | 0                                      | 1,34                      |
| 4  | CNT 0.5% + NTF 30%      | 4                                      | 1,76                      |
| 5  | Raw wood                | 184                                    | 80                        |

A comparison of the fire-retardant properties of wood when modified with a sandwich coating of CNTs and NTFs is shown in Figure 2.
Figure 2. Indicators of mass loss during the modification of the sandwich coatings of CNT + NTF

As can be seen from table 2, sandwich coatings increase the fire resistance of wood by 5-6 times. CNTs have practically no effect on the fire resistance of wood without organophosphorus antiperen. Figure 2 shows that the effect of the concentration of CNTs on mass loss is not linear. The most effective are the concentration of CNT 0.1-0.5%. The surface of the samples with sandwich coatings is characterized by the unevenness of the outer layer of CNTs. For low concentrations of CNTs, some unevenness of the coating is characteristic of concentrations of CNTs of 0.01-0.05%. Regular coatings are typical for a concentration of 0.1%. Figures taken using a dual beam electron microscope Dual Beam modified wood surfaces are presented in figures 3-7.

Figure 3. Elemental analysis of CNT 0.01% + NTF 30%; C = 54%, P = 1.37%
Figure 4. Elemental analysis of CNT0.1% + NTF30%: C = 57%, P = 1.34%

Figure 5. Elemental analysis of CNT0.5% + NTF30%: C = 35%, P = 15%
Figure 6. Elemental analysis of CNT0.05% + NTF30%: C = 45%, P = 2.5%

Figure 7. Elemental analysis of CNT1% + NTF30%: C = 47.3%, P = 4.4%
According to the obtained images, an analysis was made of the relationship of fire-retardant properties with surface characteristics, which is presented in table 3.

**Table 3.** The results of a study of the structure and chemical composition of the surface layer of modified wood.

| No | Composition       | Surface structure          | Elemental composition | Mass loss Δm, % |
|----|-------------------|----------------------------|-----------------------|-----------------|
| 1  | CNT 0.01% + NTF 30% | No uniform coverage       | C=54%, P=1.37%        | 2.82            |
| 2  | CNT0.05% + NTF30% | Uniform capillary coating | C=45%, P=2.5%         | 2.4             |
| 3  | CNT0.1% + NTF30%  | No coating continuity     | C=57%, P=1.34%        | 1.34            |
| 4  | CNT0.5% + NTF30%  | Separate areas of opaque coatings | C=35%, P=15%          | 1.24            |
| 5  | CNT1% + NTF30%    | Uniform coating           | C=47.3%, P=4.4%       | 3.2             |

### 3. Results and discussion

As can be seen from table 3, the uniformity of the coating does not enhance the fire retardant properties. The data of the FOS elemental analysis do not allow one to derive unambiguous dependences of the mass loss on the nature of their chemical composition of the surface.

An increase in the percentage of CNT content increases the mass loss with the data obtained allows us to draw the following conclusion: when modifying the surface of the concentration of CNTs in a sandwich coating, the values should be in the range of 0.1-0.5%. In this case, the formation of chemical bonds of CNTs with the reaction components of flame retardants occurs, and the concentration of CNTs is 0.1-0.5%. A greater number of carbon-containing components increases the flammability of the surface.

A study of the hydrophobic and strength properties of wood samples modified with FOS and CNT sandwich coatings of 0.1-0.5% showed that wood coatings with these compositions increase water resistance by 30%, and compressive strength across the fibers increases by 20%.

The effect of the concentration of FOS and CNTs in the sandwich coating of modified wood on its combustibility parameters and other characteristics was studied.

Modifications of the wood surface in a thin layer with nanodispersed composites transfers wood to the category of hardly combustible materials with increased strength by 20% and water resistance by 30%, while the content of CNTs should not exceed 0.5%.

### 4. Conclusions

The effect of the concentration of FOS and CNTs in the sandwich coating of modified wood on its combustibility parameters and other characteristics was studied.

Modifications of the wood surface in a thin layer with nanodispersed composites transfers wood to the category of hardly combustible materials with increased strength by 20% and water resistance by 30%, while the content of CNTs should not exceed 0.5%.

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