

Physics and chemistry of creation of fire protection and bio protection by modification of thin surface layers

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Abstract. An innovative use of wood structures is the creation of high-rise buildings. This is a promising direction in construction in many countries: USA, Australia, Canada, England, etc. Wood (timber) is a material created by nature. Energy consumption for creation of wood structures is a lot smaller in comparison with polymer, glass, or aluminum structures. This causes the economic and energy efficiency of wood building materials. The research has identified the nature of modifiers and the surface modification conditions in thin surface layers (0.5-1 mm). This is important, since this approach does not lead to increase of the weight of the structure, which is very important in conditions of high-rise construction. Mechanism and kinetics research allowed to select the efficient modifiers. Element analysis and infrared spectroscopy was used in the research to evaluate the effectiveness of wood modifying. Influence of the surface layer structure on the modification have been analyzed using the chemical thermodynamics, adsorption, and electron microscopy methods. For research samples we used the pine, which widely used in construction, and samples taken from the memorial wooden architecture, which allow you to assess the durability of structures. It was determined that the most efficient in surface thin layer modification are the esters of phosphorous and phosphinic acids. Wood structures modified wood had group I fire protection efficiency (loss of weight during the fire protection efficiency test was 5 - 9.5 %). Biostability has been analyzed in Severtsev Institution of RAS RF. Results have demonstrated that the wood structures materials analyzed are biologically stable.

1. Introduction

Today's multi-story timber construction is relevant and innovative. Buildings can have 9, 13, and 20 stories. In Austria, a settlement with 9- and 13-story timber-frame houses was built. Designing and erecting timber-frame buildings is underway in the Russian Federation, the USA, Canada, and Finland. The use of timber structures in today's multi-story construction is based on the innovative properties of timber. Timber is a material created and reproduced by nature. The cost of energy in the production of timber frames is ten times less than that of polymers and aluminum. This explains the economic and energy efficiency of timber frames, including in the construction of high-rise buildings[1-3].

The drawback of timber structures is flammability and susceptibility of bio-corrosion. Enhancing the fire- and bio-resistance of timber structures of high-rise buildings by modifying thin surface layers is a vital task. MSGU (Moscow State University of Civil Engineering) has developed a method of soft timber surface modification. With soft surface modification, chemical bond of the substrate with a modifier is



formed at of 20-25 °C, resulting in a new material with stable, long-lasting fire- and bio-resistance[4-10].

In multi-story timber construction, it is required to use compositions, whose effectiveness is manifested with a thin-layer coating; the thickness of the layer being 0.5-1 mm. Increased thickness of the protective layer tends to increase the weight of the structure.

2. Materials and methods

The research was based on samples of pine timber (sapwood). Having studied published references, we chose dimethyl phosphite 20% as a modifier [11-12]. The degree of chemical interaction of the modifier with the timber surface was measured with Quanta-200 scanning microscope with Apollo-40 elemental analysis attachment using energy dispersive spectroscopy. The percentage of phosphorus was measured in the surface layers of 0.5-1 mm.

The surface of the original and modified timber was examined using an electronic microscope JSM-840. The energy bond of dimethyl phosphite modifier with the timber surface was explored using Magna-750 Fourier spectrometer from Nicobet (USA) [13-15].

The fire- and bio-proof properties of the modified layer were determined on the basis of GOST standards. The combustibility group of materials was identified under GOST 12.1.044-89. The fungal resistance of the modified timber was measured in accordance with GOST R 53292-2009.

The kinetics of surface phosphorylation of timber treated with dimethyl phosphite was explored by the method of dispersive kinetics with the determination of the activation energy E (kcal/mol) and the rate constant K_0 (s^{-1}).

3. Results and discussion

The permeability of the composition in timber samples through surface modification was determined using the percentage of phosphorus (Figure 1, Table 1).

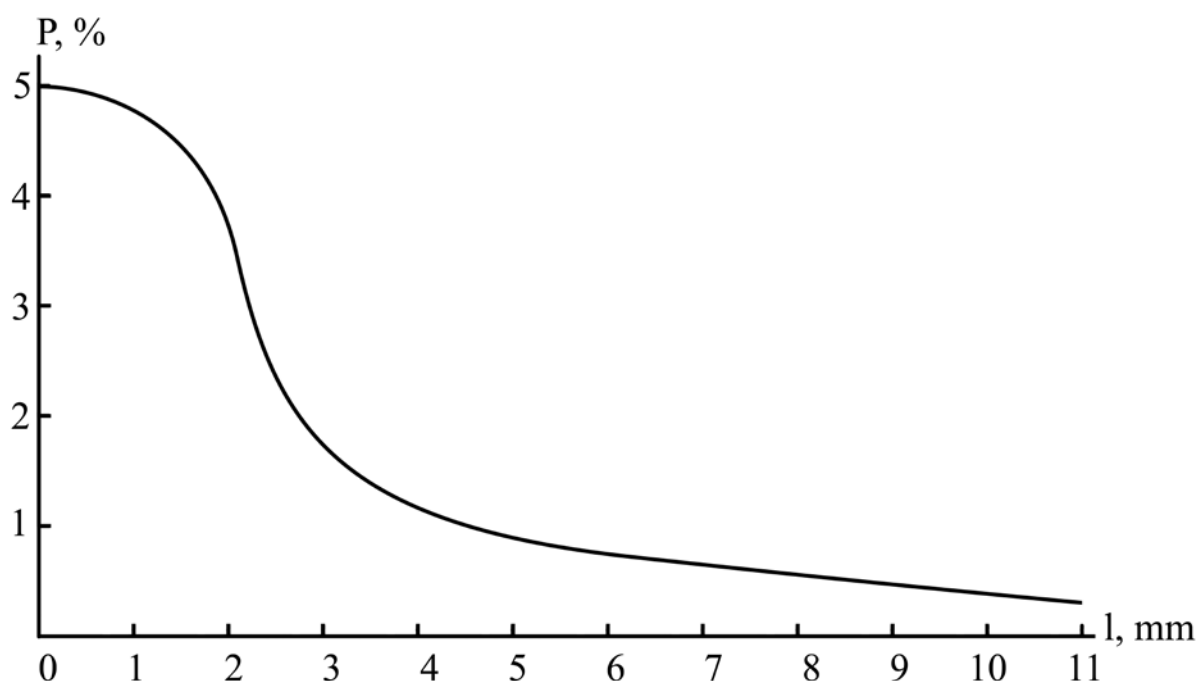


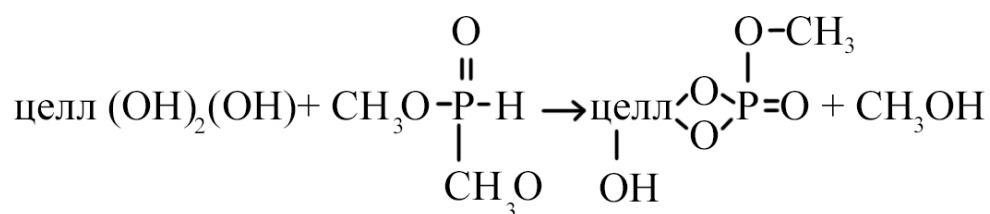
Figure 1. Dependence of the phosphorus content in timber on the permeability of the protective composition of dimethyl phosphite

We explored samples 2x2x2 mm taken from the surface of the sample modified with 20% dimethyl phosphite. Figure 1 and Table 1 show that with surface modification, the density, and, consequently, the weight of the structure does not increase substantially, which is crucial for high-rise buildings.

Table 1. The change in the density of timber after surface modification with dimethyl phosphite

l, mm	The density of investigated material	
	The original timber	Timber modified by DMF
0.1	0.460	0.460
0.9	0.480	0.480
2.0	0.480	0.481

The interaction of phosphorous acid esters with timber (cellulose) is described by the reaction (Figure 1):

**Figure 2.** The reaction of the interaction of phosphorous acid esters with timber

The kinetic parameters were measured according to the principles of dispersive kinetics. Table 2 and table 3 shows that the phosphorylation of timber surface after dimethyl phosphite treatment is diffusive, that is, the modification can occur at about 20 °C higher, which is important for the protection of timber structures. With thermal decomposition of modified timber, the percentage of coke grows, which enhances the fire resistance of timber [16-17].

Table 2. The kinetic parameters of timber phosphorylation by DMF

E, kcal/mol	K ₀ , s ⁻¹	% P
3.8 - 9.6	-1.5	3.3

Table 3. The kinetic parameters of thermal decomposition of the original timber and timber modified by DMF

Condition of wood	E, kcal/mol	K ₀ , s ⁻¹	Proportion of coke
Moditied by DMF	32.14	3.8·10 ⁻³	0.48
Original wood	47.40	5.7·10 ⁻⁶	0.40

The surface layer of modified timber was studied by electron microscopy (Figure 3, Figure 4, and Figure 5).

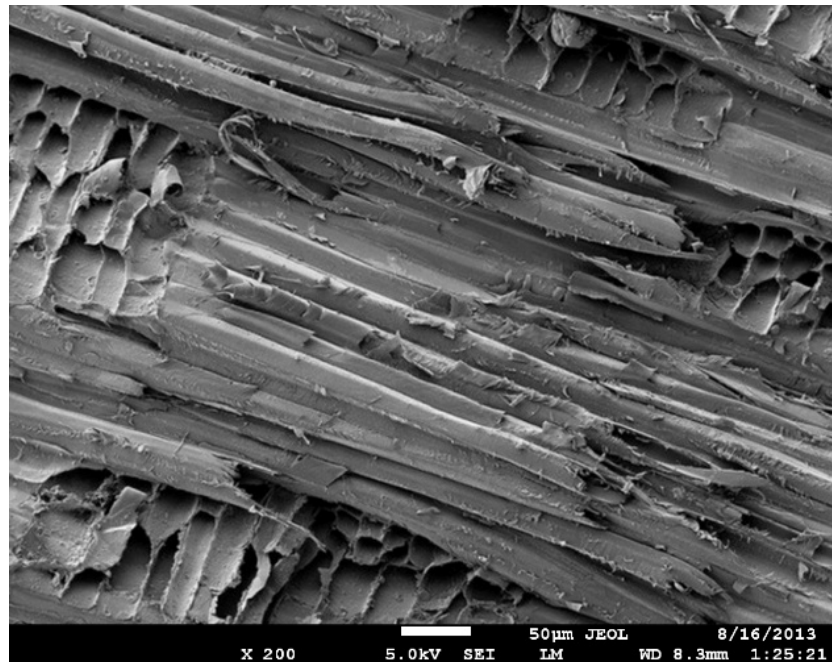


Figure 3. Photographs of original timber surface obtained through electron microscopy with 100x magnification

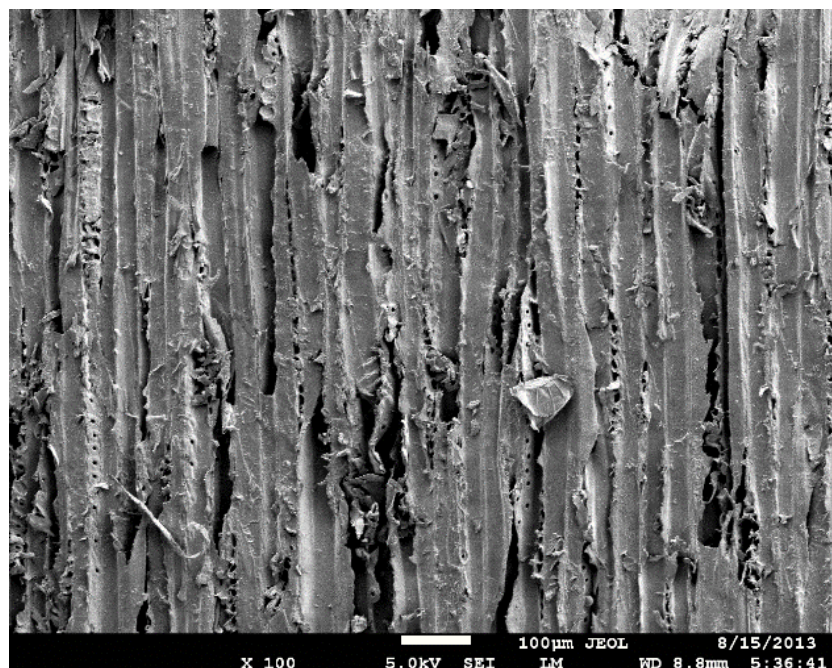


Figure 4. Photographs of timber surface modified by DMF obtained through electron microscopy with 100x magnification.

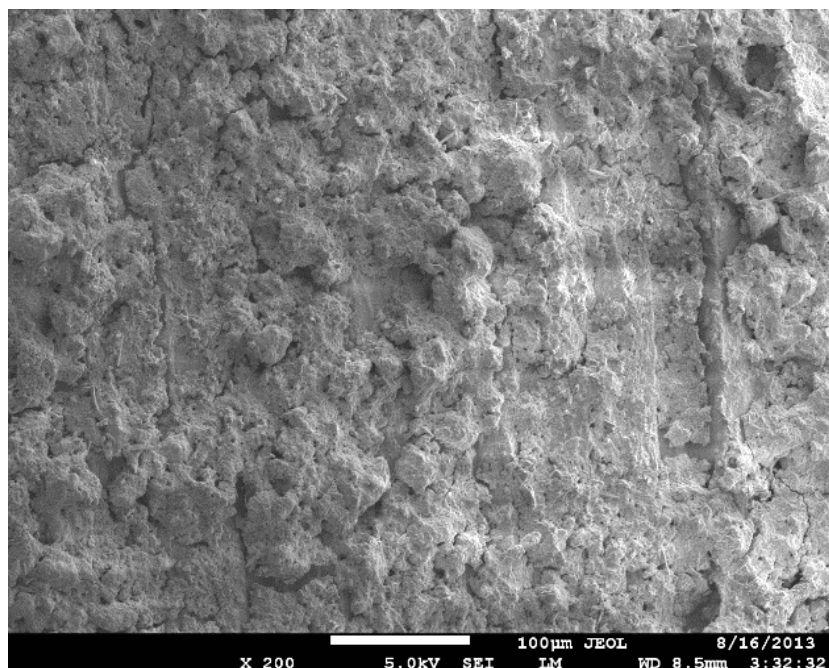


Figure 5. Photographs of timber surface modified by PFA-1) obtained through electron microscopy with 100x magnification

The photos show that the timber, whose surface was modified with dimethyl phosphite, has a regular structure, which characterizes the interaction of the modifier with the substrate (Figure 4). The coating with ammonium polyphosphate has a chaotic nature, which demonstrates the lack of regular chemical bond.

Table 4 and table 5 shows the results of tests on the definition of the fire-resistance rating and resistance to fungi of modified timber.

Table 4. Fire-hazardous properties of the original and modified timber

Condition of wood	Weight loss, %	A group of fire-resistance rating
Original wood	79.0	I
Moditied by DMF	5.9	III

Table 5. Bio-proof efficiency of thin-layer dimethyl phosphite coating (GOST 9.048-89)

Condition of wood	Surface appearance after tests	biological damage ball	Biostability, %
Original wood	80% of the surface is infected by fungi	5	0
Moditied by DMF	the absence of fungi	0	100

4. Conclusions

The physical and chemical study of the thin-layer treatment modifying timber surface helped to draw the following conclusions.

A dilute aqueous solution of dimethyl phosphite, when applied superficially at a permeability of 0.5-1 mm, enters into a "soft" chemical modification with timber components. This results in phosphorylated cellulose products. As a result of chemical modification, timber and its components acquire new durable properties. Timber acquires fire rating of Group I under GOST 16363-89 ($\Delta m = 5.9\%$).

Timber becomes bio-proof. Here, the thin-layer surface treatment does not increase the density of timber and actual weight of the structure, which is important for high-rise timber housing construction.

To sum up, we can make the following generalization. For fire- and bio-proofness of timber structures in high-rise housing construction, fire retardants are used, which in aqueous (or organic) solutions form a thin film on the surface of the substrate (0.1-0.2 mm). In this case, the fire retardant must react with the components of the timber at 20-30 °C. The degree of interaction is determined by 1.5-3.8% chemically bound phosphorus for phosphorus-containing flame retardants.

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