Decrease in Swelling Capacity of Pine Wood Modified with Aminoborates

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Abstract. Upon direct contact of wood with water, a hydrophilic hydroxylated substrate actively absorbs water molecules due to the capillary-porous structure of the wood. Since water is characterized by high dielectric permittivity, sorption of water is usually accompanied by the swelling of the wood. It leads to the deterioration of the physical and the mechanical properties of the wood composite and, when the surface is covered with a film of paintwork materials while the wood is not subjected to an appropriate treatment, the pressure of the constrained swelling can cause destruction of the substrate. We have established in our work that the modification of the pine wood with the aqueous solutions of aminoborates leads to a decrease in the equilibrium degree of swelling, with 50 % modifier solutions being the most effective in this respect. In this study, the swelling rate of the substrate was found to be inversely proportional to the concentration of the modifier — with an increase of the concentration of the modifiers the swelling rate was markedly reduced due to the rate constants decrease. The results obtained allow us to speak of a decrease in swelling capacity of pine wood modified with aminoborates.

1. Introduction
Being a natural capillary-porous fibrous composite material, which amorphous matrix (lignin) is reinforced with one-dimensional fillers – cellulose and hemicellulose macromolecules [1] rich in hydroxyl groups, wood is characterized by high water absorbing capacity [2]. Water penetrates into the wood fibers and loosens the fiber structure as it loosens the micellar rows and breaks the hydrogen bonds between hydroxyl groups of adjacent molecules [3, 4]. Since water has high dielectric permittivity, water sorption is usually accompanied by wood swelling [5]; so the physical and mechanical properties of the wood composite deteriorate. Swelling pressure in a confined space results from the counterstand of the wood components having insufficient space for unconstrained swelling. Such components include hemicelluloses enclosed between microfibrils and pectic substances localized in the middle lamella [6]. Swelling pressure can cause destruction of the substrate if the surface is covered with a film of paintwork materials while the wood is not subjected to an appropriate
treatment [7, 8]. The task of reduction of the wood swelling capacity upon contact with water is therefore of importance.

To reduce the swelling of wood fibers, special additives are introduced into the impregnating mixtures, for example, alcohols [9]. A waterborne paint for finishing of coniferous wood was developed in the Laboratory of Finishing of the Siberian State Technological University [10]. These waterborne paints provide a uniform coating on wood with pronounced anisotropic properties and do not lead to swelling. Coating is formed as a result of paint coagulation on the substrate (removal of the major part of water to form the intermediate gel, syneresis of the intermediate gel, autohesion processes). A microfilm ensuring a uniform color is formed on the surface due to the presence of a lyophilic film-former in the composition. At the same time, the wood texture is masked and the wood unique properties are diminished: abilities to absorb harmful impurities from the air, to maintain the optimal humidity, to saturate the air with natural antiseptics such as resins and essential oils are leveled off.

The cellulose supramolecular structure is ordered, the wood specific surface and its water sorption capacity decreases upon modification with aminoborates [11-14]. We assumed that modification of pine wood with aqueous solutions of monoethanolamine(N→B)-threehydroxyborate and diethanolamine(N→B)-threehydroxyborate would lower the equilibrium degree of swelling, which along with good antiseptic properties of aminoborates would provide durability to wooden structures and buildings.

2. Methodology

Samples of pine wood in the form of a rectangular prism (20 × 20 mm base and 10 mm height along the fibers) were used as the subject of the study. Aqueous solutions of aminoborates: 10 %, 30 %, and 50 % monoethanolamine(N→B)-threehydroxyborate (MEAB), diethanolamine-(N→B)threehydroxyborate (DEAB), were used as modifiers.

Modifier solutions were applied to the surface of the wood samples with a brush followed by drying of the modified samples to constant weight at room temperature. The dry modified samples were immersed in water and the degree of swelling was evaluated by the gravimetric method. Degree of swelling α was calculated according to Equation (1):

$$\alpha = \frac{m - m_0}{m_0};$$

where

- $m_0$ – weight of the sample, g;
- $m$ – weight of the swollen sample at equilibrium, g.

The swelling kinetics is described by kinetic curves plotted in coordinates $\alpha = f(t)$. The plateau on the curves obtained corresponds to the equilibrium degree of swelling, i.e. its maximum value.

The process of wood swelling is determined by the rate of water molecules diffusion and the swelling rate can be described by the following Equation (2):

$$\frac{d\alpha}{dt} = k(\alpha_{\text{max}} - \alpha_t);$$

where

- $\alpha_{\text{max}}$ – equilibrium swelling degree,
- $\alpha_t$ – swelling degree at time $t$.

Integrating the last equation, we obtain (3), (4):

$$k = \frac{1}{t} \ln \frac{\alpha_{\text{max}}}{(\alpha_{\text{max}} - \alpha_t)};$$

or

$$k = \frac{1}{t} 2,3 \lg \frac{\alpha_{\text{max}}}{(\alpha_{\text{max}} - \alpha_t)};$$

Plotting it as a function $2,3 \lg \frac{\alpha_{\text{max}}}{(\alpha_{\text{max}} - \alpha_t)}$ of $t$, we obtain a straight line whose slope is equal to the swelling rate constant $k$ of wood in water.
3. Results and discussion
The swelling kinetics of the test samples in water is described by kinetic curves, Figure 1. It can be seen that the swelling process gradually slows down and reaches the plateau at the maximum (equilibrium) value of the swelling degree. The equilibrium swelling degree of the unmodified wood sample is 1.31 (131%), the sample treated with MEAB - 0.89 (89%), and the sample treated with DEAM - 0.68 (68%).

It is known from the literature that the equilibrium swelling degree depends on the ability of the wood to absorb and retain a certain amount of water. There are two types of sorption centers with different binding energies. Primary centers of sorption include hydrophilic groups of cellulose, hemicelluloses and lignin [15, 16]. Secondary sorption centers are the centers of sorption of the first and subsequent layers of water. Primary sorption centers actively absorb water and water molecules are directly linked to -OH groups of amorphous regions of wood macromolecular components. This process is exothermic. It leads to a significant decrease in the total energy of the "water-wood" system due to the sorption heat release [17, 18].

Formation and retention of the second and subsequent adsorption layers takes place due to the dipole-dipole interaction between the water molecules. These processes are associated with the release of ordinary dilution heat, which, along with the increasing role of the entropy factor, limits the rate of sorption processes and limits the amount of absorbed water [19, 20]. Consequently, the more primary sorption centers available, the greater the swelling capacity of wood.

Lower values for the equilibrium swelling degree of the modified wood result from an increase in the crystallinity degree of the cellulose after wood modification. This is also facilitated by the formation of a more rigid spatial network of reinforcing wood components due to the interaction of the modifier molecules with hydroxyl groups of C6 and C2 carbon atoms of the glucopyranose ring of adjacent cellulose chains.

The swelling rate constants for samples of modified and unmodified wood were determined graphically as the slope of the straight line plotted in the coordinates $2.3 \times \log(\alpha_{\text{max}}/(\alpha_{\text{max}} - \alpha)) = f(\tau)$, Figure 2. The swelling rate constants for the "unmodified wood — water", "wood+MEAB — water", and "wood+DEAB— water" systems were 0.075, 0.061, and 0.079, respectively.

The obtained values of the swelling rate constants point to the absence of a direct correlation between the swelling rate and the saturation limit. The swelling rate constant of wood modified with
diethanolamine(N→B)-threehydroxyborate is higher than that of unmodified wood. This might be due to the manifestation of capillary condensation forces. The specific surface area of the modified wood is reduced, which causes the negative capillary pressure increase, and, consequently, increases the water absorption rate of the modified wood.

The swelling rate constant of wood modified with MEAB is lower than the swelling rate constant of unmodified wood. We assume that higher graft density of the modifier and its ability to interact with adjacent cellulose macromolecules causes crystallinity to increase and creates additional steric barriers for water molecules penetration into the bulk of the wood composite.

To determine the optimum concentrations of the modifiers, equilibrium swelling degrees were determined for wood samples modified with 10 % and 30 % solutions of mono- and diethanolamine (N→B)-threehydroxyborates. As follows from the experimental data obtained for the 10 % and 30 % solutions of modifiers (Table 1), as the concentration of the modifiers decreases, the ability of the modified wood to swell increases. The equilibrium swelling degree in all samples of modified wood is below control. The equilibrium swelling degree is lower for wood samples modified with MEAB, than for wood samples modified with DEAB, which may be attributed to the lower reactivity of DEAB.

**Table 1.** Experimental and calculated values for wood samples modified with 10 % and 30 % modifier solutions

| Swelling time t, days | α     | 2,3*lg(α<sub>max</sub> / (α<sub>max</sub> - α)) | Swelling time t, days | α     | 2,3*lg(α<sub>max</sub> / (α<sub>max</sub> - α)) |
|----------------------|-------|-----------------------------------------------|----------------------|-------|-----------------------------------------------|
|                      | Wood + MEAB |                                              | Wood + MEAB |                                              |
| 0                    | 0     | -                                             | 0                    | -     | -                                             |
| 1                    | 0,51  | 0,66                                          | 1                    | 0,36  | 0,51                                          |
| 3                    | 0,57  | 0,77                                          | 3                    | 0,43  | 0,65                                          |
| 6                    | 0,65  | 0,95                                          | 6                    | 0,54  | 0,92                                          |
| 9                    | 0,68  | 1,02                                          | 9                    | 0,59  | 1,06                                          |
| 13                   | 0,77  | 1,29                                          | 13                   | 0,64  | 1,24                                          |
| 20                   | 0,94  | 2,18                                          | 20                   | 0,78  | 2,01                                          |
| 30                   | 1,06  | -                                             | 30                   | 0,9   | -                                             |
| 40                   | 1,06  | -                                             | 40                   | 0,9   | -                                             |
Wood + DEAB

| 10 % DEAB solution | 30 % DEAB solution |
|---------------------|--------------------|
| 0                   | 0                  |
| 1                   | 0,45               |
| 3                   | 0,53               |
| 6                   | 0,78               |
| 9                   | 0,83               |
| 13                  | 0,99               |
| 20                  | 1,07               |
| 30                  | 1,19               |
| 40                  | 1,19               |

As the concentration of MEAB decreases, the swelling rate constant of the modified wood increases (Figure 3). This might be attributed to the lower graft density and less influence of the
modifier on the crystalline structure of carbohydrates of the wood composite. As the concentration of DEAB decreases, the swelling rate constant also increases. However, the swelling rate constant of unmodified wood is lower than that of the modified samples at all modifier concentrations. This may be explained by the peculiarities of the DEAB structure: the introduction of bulk modifier molecules to the primary centers of wood sorption creates favorable conditions for the formation of the second and subsequent water adsorption layers.

4. The conclusions
The following conclusions can be drawn based on the obtained results. Modification of wood with aqueous solutions of mono- and diethanolamine(\(\text{N} \rightarrow \text{B}\))-threehydroxyborates reduces the wood swelling capacity and leads to the equilibrium swelling degree decrease. The swelling rate constants depend on modifier type and concentrations. The swelling rate of the modified wood decreases with increasing concentration of the modifiers, and the most effective are 50% solutions. The swelling rate constants of wood modified with MEAB are below or at the level of the swelling rate constant for the unmodified wood. This may be explained by the significant influence of the modifier on the supramolecular structure of cellulose. The swelling rate constants of wood modified with DEAB are higher than the swelling rate constants for the unmodified wood, which may be explained by the absence of steric hindrances in the "dipole-dipole" interaction of water molecules with secondary centers of wood sorption.

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