Stabilization of shapes and dimensions of compressed wood using chemical and physical methods

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Abstract. Descriptions of methods and results of experiments on the preservation of geometry and dimensional parameters of compressed wood using chemical and physical methods are given. Wide ranges of substances were used as chemical stabilizers in urea aqueous solution (plasticizer during pressing). Wood treatment with ultrasound, liquid nitrogen and pulsed magnetic field was used as physical methods. Urotropine, urea-formaldehyde oligomer, phenol-formaldehyde resin, butyric anhydride and physical methods (liquid nitrogen and pulsed magnetic field), as well as ultrasound can be applied to increase form stability of pressed wood to the level of swelling in water and water absorption of natural wood (respectively, 15-20% and 30-45%). Cashew nut shell liquid is recommended to obtain stable pressed wood. The liquid, with a content of 6-12% (by dry residue) relative to the mass of dry wood during heat treatment in the temperature range of 150-155°C for 8 hours, gives limiting volume swelling 7-8% and limiting water absorption 14-18%. Fully stable compressed wood was obtained after exhaustive acetylation with acetic anhydride and subsequent maximum impregnation with phenol alcohols (more than 70% of content) and thermocatalytic curing. However, this method cannot be recommended due to high toxicity and material weakness.

1 Introduction

The current level of technology indicates that methods are being developed to stabilize shapes and sizes of natural (solid) wood in the environment with high humidity [1-3]. Acetic anhydride, polyethylene glycol, polyvinyl alcohols are used as stabilizing components of wood. Hydro-thermal treatment is also used [4,5]. The most promising modification method is wood pressing [6-8]. However, this method has a significant drawback: increased formability. The swelling of the pressed material is 7–10 times higher than that of natural wood. Nevertheless, there are developments in this direction. They are effectively used to preserve the geometry and dimensional parameters of compressed wood [9-11]. In Russia, China and other countries, the processes of applying technologies for saturation of soft

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hardwood with an aqueous solution of carbamide in combination with pressing and drying [12] are developing dynamically. The resulting product acquires physical, mechanical and decorative properties of such species as oak, mahogany and boxwood. To ensure the stability of geometric shape and dimensions, additives are also used increasing the effectiveness of the formation processes of carbamide bonds with wood components. For example, urotropine (hexamethylentetramine) is used for these purposes [13].

2 Experimental part

Using the method of processing wood with carbamide and urotropine, wood is impregnated with a solution of urea, obtaining a dry weight content of 10–15%. This technique is described in detail in our patent [14]. A similar stabilization result is achieved by using a urea-formaldehyde oligomer (UFC) pre-condensate, using the method of processing wood with urea-formaldehyde oligomer (described in detail in our patent [15].

Instead of UFC, an aqueous solution of maleic acid can be used for impregnation (method of wood treatment with maleic anhydride). This provides simplification of the technology. This technique is described in detail in our article [16]. Table 1 shows the properties of compressed wood.

Table 1. Characteristics of modified material.

Indicators	Value
Content of modifying agent, %	12-13
Treatment temperature,°C	160-165
Density, kg/m^3	1 250-1 260
Swelling in water in 30 days (volumetric), %	7.8
End surface hardness, MPa	159-161

In the course of the study, it was found that maleic acid, in combination with the pressing process, provides wood modification with an increased density and with a volumetric swelling of no more than 10%. As a result, effective protection against water is provided and form stability of products is increased.

Method of wood processing with phenol-formaldehyde resin SFZh-3014K, pre-condensate urea-formaldehyde resin UFC-85, cashew nut shell liquid (CNSL). Wood blanks of birch (*Betula verrucosa L*) and alder (*Alnus glutinosa*), 80×80×120 mm in size (the last dimension along the fibers), were impregnated separately with SFZh-3014K, UFC-85 and CNSL (CNSL was acidified with "glacial" acetic acid to pH - 6.5). Impregnation was carried out in an autoclave at a pressure of 1.2 MPa for 3–5 min. After that, the specimens were dried at a temperature of 80 °C for 8 hours to a moisture content of 16-20% and pressed in a mold at a temperature of 100 °C to a degree of pressing of 25% in the radial direction, while the height of the specimen decreased from 80 mm to 60 mm. After that, the specimens were dried at a temperature of 110 °C for 6 hours and subjected to heat treatment at a temperature of 160 °C for three hours to cure and polymerize the stabilizers.

Specimens of 15×15×22.5 mm in size (the last dimension was along the fibers) were cut from pressed blanks according to The Russian State Standard 54577-2011 “Modified wood. Specifications". The specimens were tested for water absorption, volumetric swelling during

water absorption and compressive strength along the fibers [16]. Table 2 gives the characteristics of modified wood specimens. Six specimens were used for each type of test.

Table 2. Characteristics of modified wood specimens.

Stabilizer	Stabilizer content before drying and pressing	Stabilizer content after drying and pressing (by dry residue)	Moisture content, %	Density, kg/m^3
SFZh-3014K	30	9	4.6	930
UFC-85	47	11	5.2	873
CNSL	31	14	5.6	947
Control (wood impregnated with UFC-85 and dried)	75	22	4.8	595

Method for obtaining wood treated with acetic anhydride and phenol alcohols was as followed. Rectangular blanks made of soft hardwood with a moisture content of 10–15% were subjected to exhaustive acetylation with an excess of acetic anhydride for 48 hours. This technique was described in detail in our article [13].

3 Results and discussion

Figure 1 shows a dependence graph of ΔV (%) of wood volumetric swelling in water for 30 days on the content of urotropine to the mass of dry urea. This method was described in detail in our patent [17].

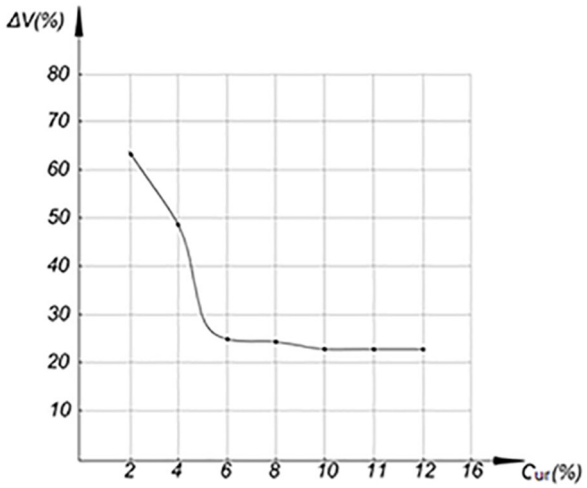


Fig. 1. Dependence of volumetric swelling ΔV on urotropine concentration C_{ur}.

Figure 2 shows a graph of the dependence of ΔV (%) of the volumetric swelling of wood on τ (day) of the water holding time: 1 - treatment with maleic acid; 2 - treatment with urotropin.

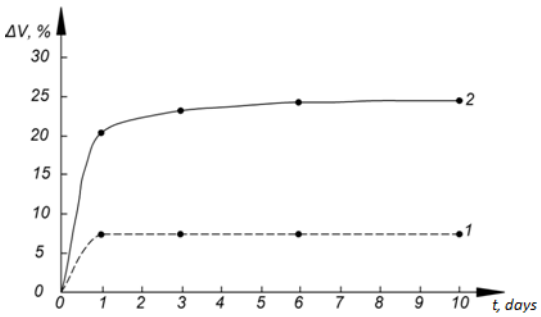


Fig. 2. Volumetric swelling of modified wood.

Tables 3 and 4 show the test results for compressed and unpressed modified wood specimens for all the stabilizers. All the stabilizers give approximately the same result in terms of water absorption and volumetric swelling for both natural and pressed wood. UFC-85 is preferable for natural wood, SFZh-3014K - for pressed wood. In general, the results cannot be called satisfactory. Heat treatment mode (160 °C, 3 hours) was selected for the previously used stabilizers, and it should be differentiated separately for each stabilizer. Let's show it on the example of CNSL. The optimum curing temperature is 150-155 °C for complete polymerization of CNSL, and CNSL decomposes at a higher temperature. The optimal processing time is 8 hours.

Table 3. Characterization of birch and alder specimens (not pressed) after tests for water absorption, volumetric swelling and compressive strength along the fibers.

Modifier and tree species	**Water absorption (limiting), %**	**Volumetric swelling (limiting), %**	**Tensile strength (compression along the fibers), MPa**	**Density, kg/m^3**
SFZh-3014K, birch	42.0	12.7	101.9	672
UFC-85, birch	26.0	10.15	70.4	642
CNSL, birch	34.0	12.1	71.8	679
UFC-85, alder	30.0	6.3	79.2	586

Table 4. Test results of pressed birch specimens.

Modifier and tree species	**Water absorption (limiting), %**	**Volumetric swelling (limiting), %**	**Tensile strength (compression along the fibers), MPa**	**Density, kg/m^3**
SFZh-3014K	52.0	22.0	117.3	961
UFC-85	72.0	38.0	82.5	852
CNSL	69.0	28.0	85.6	922

Figures 3 and 4 show the dependence of volumetric swelling in water for 30 days and water absorption of specimens on the content of the stabilizer in terms of dry residue in relation to the mass of dry wood. The specimens were impregnated with CNSL and heat-treated at a temperature of 150-155 °C for 3 hours.

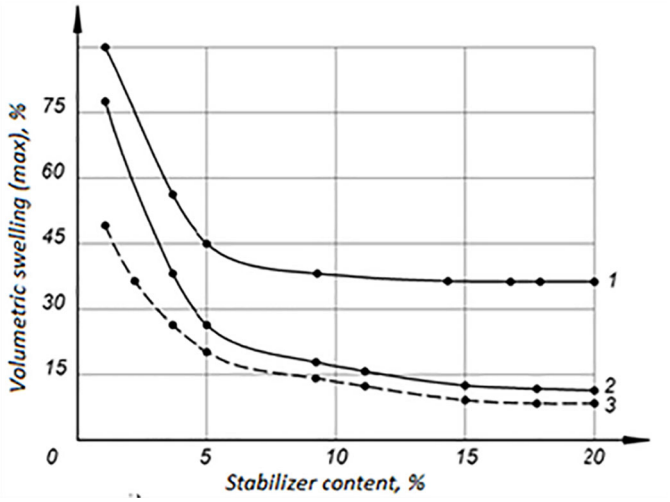


Fig. 3. Dependence of max volumetric swelling on the content of the stabilizer in the wood: 1 - urea-formaldehyde oligomer UFC - 85; 2 - CNSL, 3 - phenol-formaldehyde resin SFZh-3014K.

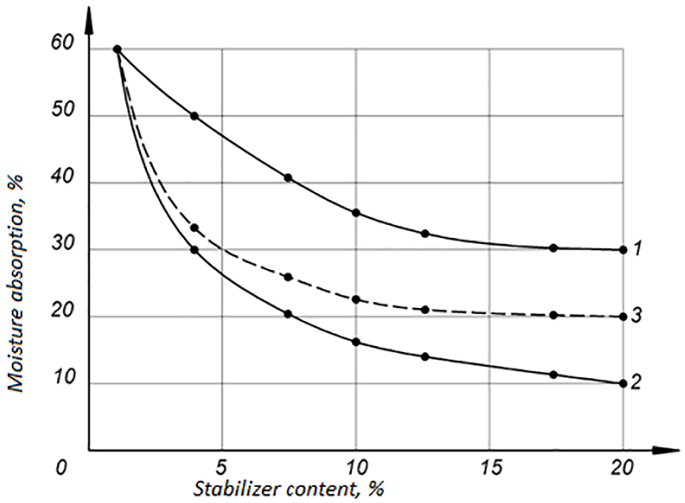


Fig. 4. Dependence of limiting water absorption on the stabilizer content in the wood: 1 - urea-formaldehyde oligomer UFC-85; 2 - CNSL, 3 - phenol-formaldehyde resin SFZh-3014K.

Figure 3 shows that limiting volumetric swelling of wood modified with 6-12% SNLC has a volumetric swelling in water of 7-8%, and a limiting water absorption of 14-18%. These characteristics enable it to compete with such brands of stabilized wood as Accoja and Kebony. It should be expected that after optimizing the polymerization modes of the UFC-85 urea-formaldehyde condensate and SFZh-3014K phenol-formaldehyde resin, similar results can be obtained.

The considered methods are examples of chemical stabilization. The combined effect of physical fields of magnetic nature in a pulsed mode and continuous cooling field allows us to obtain important results. Our assumption is based on the idea that under conditions of cryogenic temperatures, new physical bonds arise. Therefore the rigidity of molecular chains,

forming the wood skeleton, increases. When a weak pulsed magnetic field is applied, these bonds increase with increasing temperature and create a new characteristic - transition to hydrogen bonds. For this reason, the system of these bonds provides an increase in the hydrophobic properties of the treated wood. For the experiments, the wood of birch (Betula verrucosa L) and alder (Alnus glutinosa), harvested in the Ramon forestry of the Voronezh forestry enterprise, was used. The wood was processed with a pulsed magnetic field. This technique is described in detail in our article [18]. Figure 5 shows the data on the treatment of pressed wood with liquid nitrogen and weak pulsed magnetic fields (PMF).

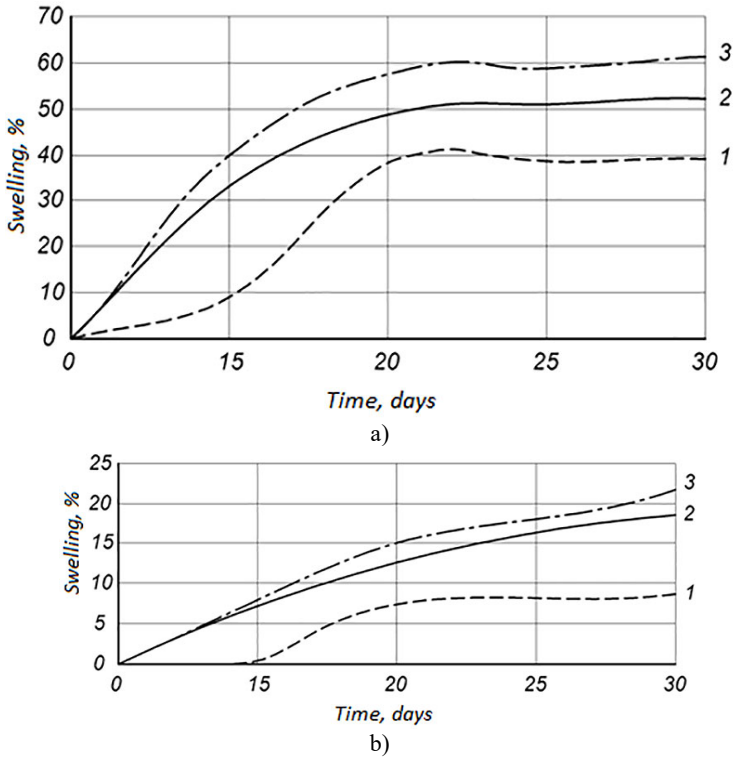
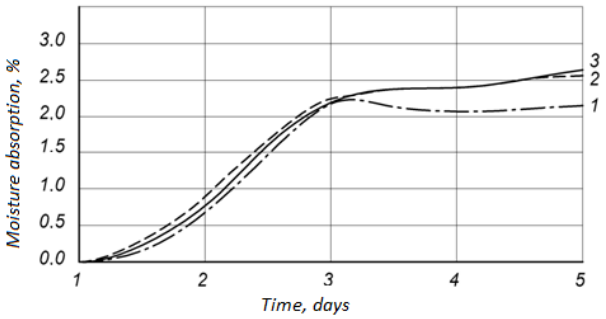
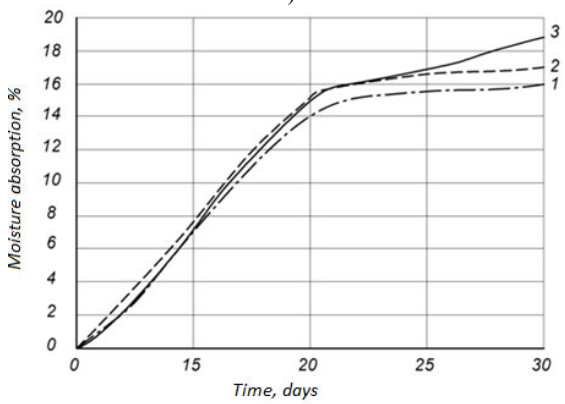


Fig. 5. Dependence of linear swelling in the direction of pressing of modified wood with water (a) and moisture (b) absorption on time: 1 - treatment with liquid nitrogen and PMF; 2 - PMF processing; 3 – natural wood.

For pressed wood, the swelling time is approximately 20 days. Including the amount of swelling of wood without exposure to physical fields - 60%, after exposure to a pulsed magnetic field - 50%, exposure to a pulsed magnetic field and liquid nitrogen - 40%, that is, the ratio is 60-50-40. For 10 days, the swelling process gives a different proportion of 35-30-5, and for 15 days - 40-33-9. What is the reason for such a big difference between wood exposed to thermal and magnetic fields and without this effect? The fact is that swelling is prevented by the formed hydrogen bonds, which gradually collapsed by the end of 15 days. For this reason, the swelling curve has a more familiar shape after 15 days. At the same time, the limiting swelling value of 40% reveals the fact that about half of the new bonds are still retained. This confirms the process of swelling during moisture absorption (Figure 6).



a)



b)

Fig. 6. Dependence of water (a) and moisture (b) absorption of modified wood on time: 1 - treatment with liquid nitrogen and PMF; 2 - PMF processing; 3 – natural wood.

Water vapor provides a low wedging effect when in contact with wood microfibrils. Pressed wood treated with a pulsed magnetic field and a low-temperature field (liquid nitrogen) has dimensional and shape stability for 15 days from the start of the process. In the limit, this value is no more than 8%. This value, respectively, is 3 times less than the value for wood without processing. This result of the constancy of sorption properties is due to the fact that chemical transformations do not occur in wood (Figures 6a and 6b). Also, an important parameter of the stability of pressed wood is its ability to restore its geometric dimensions (Table 5) when pressed out (no impact and water was removed).

Table 5. Pressing-out of wood specimens.

Physical field	**Pressing-out to original dimensions**	
	Moisture absorption	**Water absorption**
Cryogenic field (liquid nitrogen)	0.0	0.0
Pulsed magnetic field	0.79-0.8	12.8-12.9
No impact	7.85-8.0	51.6-51.8

In an environment with variable humidity, cryogenic and pulsed magnetic fields (Table 5) ensure that the wood does not decompress. That is, form stability of products reaches form

changeability of natural wood. Similar results have been achieved using a pulsed acoustic field. Ultrasonic pulse parameter was: frequency – 20 kHz, duration - 150-180 s. It helps avoid the destruction of the cellulose skeleton, which reduces the strength of wood, and ensure the melting of hemicelluloses and part of the lignin. The description of the experiment is given in detail in our patent [19]. Pressed wood under ultrasound field impact acquires hydrophobic qualities. At the same time, its swelling in water tends to a value of 12% (Table 6).

Table 6. Modified wood.

Characteristic	Value
Density, kg/m^3	790.0-800.0
Moisture content, %	19.9-20.0
Ultimate compressive strength along the fibers, MPa	90.2-90.3
Volumetric swelling at moisture absorption, %	7.9-8.0
Volumetric swelling at water absorption, %	12.0-12.1
Water absorption, max, %	29.8-30.0

Similar result can be obtained by heat treatment of wood with a pulsed magnetic field (amplitude - 0.5 T, triangular pulses, repetition rate - 50 Hz, base duration - 50 m/s) and urea-formaldehyde oligomer (UFC) with the addition of urea-formaldehyde resin PKP-52 (21 – 25% of UFC mass). The resulting modified wood has a maximum volumetric swelling in water of 7–9%, which is two times lower than that for modification with pure UFC [20]. Acceleration of oligomer polymerization process with hardener increases the degree of polymer binding with wood. Therefore, the stabilization level of the modified wood shape increases. The modifier polymer under the influence of pulsed magnetic field stabilizes the properties of wood under conditions of prolonged and periodic influence of temperature and moisture. Thermal exposure (140–160 °C) increases the rate and degree of polymerization. This improves product stability and reduces the overall energy cost of the modification process. The efficiency of hardener is shown in Figure 7: curve 1 - UFC without hardener, curve 2 - UFC with hardener.

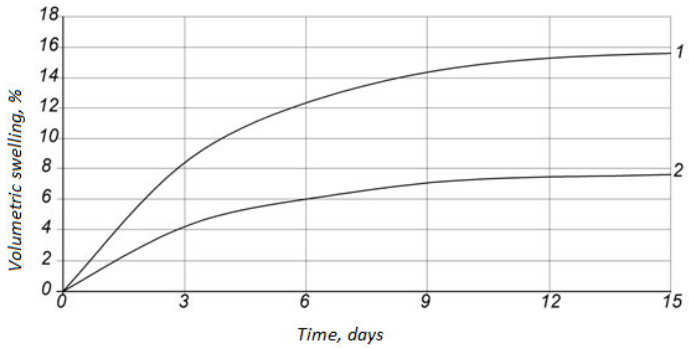


Fig. 7. Volumetric swelling of modified wood: 1-UFC; 2-UFC with hardener.

Stabilization technology is based on the use of urea aqueous solution. Urea-formaldehyde oligomer (UFO) condensate is used as an additive (10–12% by weight of dry carbamide). The technology is described in detail in our publications [21]. Thus, the resulting modified wood can have a density of 810-1090 kg/m3. In the presence of moisture, its volumetric swelling is about 7–9% (Figure 7). And this is 2 times less than in the case when hardener is not used. It is natural to ask under what conditions for an environment with variable humidity it is possible to obtain a completely stable pressed wood? The answer is to solve a complex problem: at the macro level of wood geometry, at the level of cells and at molecular level. At the macro level, the main deformations occur. When swelling, cells and cellular tubes interact with moisture and experience stress. Emerging forces tend to restore the initial form. The solution is to use a three-dimensional network formed by phenol alcohols that react with wood components. At the second level, it is important to ensure the connection of cellulose molecules to prevent displacement. A solution may be to use phenol-formaldehyde oligomers (phenol alcohols) for impregnation and curing. And at micro level, it is necessary to block the hydroxyl groups of cellulose, as well as hemicelluloses and lignin. The solution is to treat with acetic anhydride to achieve wood acetylation result. Individual and overall results of wood acetylation and its treatment with phenolic alcohols are compared in Table 7. The overall result provides 4.3% for swelling and 10.3% for water absorption.

Table 7. Properties of compressed wood, treated with acetic anhydride and phenol alcohols.

Type of wood treatment	Density, kg/m^3	Acetylation level, %	Share of phenol alcohols in wood, %	Volumetric swelling, %	Water absorption, %
Acetic anhydride	1200-1220	22.1	–	15.1	18.1
Phenolic alcohols	1010-1020	–	120	6.1	23.1
Acetic anhydride and phenolic alcohols	1200-1210	23.1	100	4.3	10.3

Comparing the data of Tables 6 and 7, we find that the overall effect of acetylation and phenol alcohols exceeds the calculated data: swelling - 7 times, water absorption - 2 times. Phenol alcohols make the greatest contribution to stabilization. Thus, the method discussed above can be used to obtain pressed wood with formability in the range of temperature changes. Since the above material has a high cost and toxicity, its use is limited (for example, specialized products of friction parts) [21-23].

4 Conclusion

Physical and chemical treatment of pressed wood ensures its shape stability up to 15-20%, water absorption - 30-45%. For this, physical (cryogenic temperature, pulsed magnetic field, and ultrasound) and chemical (urotropine, urea-formaldehyde oligomer, phenol-formaldehyde resin, butyric anhydride) methods can be used. Wood treatment with cashew nut shell liquid (CNSL) is recommended to obtain stable pressed wood. CNSL (at a content of 6-12% (by dry residue) of the mass of dry wood after heat treatment at 150-155 °C for 8 hours) gives limiting volumetric swelling of 7 -8% and maximum water absorption of 14-18% [24]. Fully stable compressed wood is obtained after exhaustive acetylation with acetic anhydride and subsequent maximum impregnation with phenol alcohols (more than 70% content) and thermocatalytic curing. However, this method cannot be recommended for use due to high toxicity and brittleness of the material.

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