ONLINE ISSN 2069-7430
ISSN-L 1841-4737
PRO LIGNO
www.proligno.ro
Vol. 11 N° 4 2015
pp. 65-72

METHODS OF CHARACTERIZATION OF MEMORY EFFECT OF WOOD

Galina A. GORBACHEVA
Moscow State Forest University, Faculty of Mechanical and Chemical Wood Technology
1st Institutskaya street, 1, Mytischi, Moscow region, 141005, Russia
Tel: +7 495 6873725, E-mail: gorbacheva-g@yandex.ru

Boris N. UGOLEV
Moscow State Forest University, Faculty of Mechanical and Chemical Wood Technology
1st Institutskaya street, 1, Mytischi, Moscow region, 141005, Russia
Tel: +7 495 6873725, E-mail: ugolev@mgul.ac.ru

Victor G. SANAEV
Moscow State Forest University, Faculty of Mechanical and Chemical Wood Technology
1st Institutskaya street, 1, Mytischi, Moscow region, 141005, Russia
Tel: +7 495 6873725, E-mail: rector@mgul.ac.ru

Serafim Yu. BELKOVSKIY
Moscow State Forest University, Faculty of Mechanical and Chemical Wood Technology
1st Institutskaya street, 1, Mytischi, Moscow region, 141005, Russia
Tel: +7 495 6873725, E-mail: belkovskiy@ro.ru

Sergei A. GORBACHEV
Bauman Moscow State Technical University, Power Engineering Faculty
2nd Baumanskaya street, 5, Moscow, 105005, Russia
E-mail: gorbachev96@yandex.ru

Abstract

Wood is a natural multifunctional material possessing shape memory effect (SME). Creation of scientific bases for the developing of bio-nanocomposite materials based on wood requires a most complete possible characterization of this dominant feature of smart materials. Different methods of characterization of shape memory allow to conduct qualitative and quantitative assessment of wood memory effect, study the nature of the frozen strains, changes in the wood structure. The frozen strains are the carrier of SME of wood. Experimental research of frozen strains in pine and beech wood samples with different deformation prehistories, comparative assessment of the ratio of frozen strains by different techniques (deformative conversions, quantities, thermomechanical spectrometry) were carried out. It was shown, that reversible shape changes, typical active movement phenomena are explained by the transformation of molecular-topological structure of the wood.

Key words: *natural multifunctional materials; shape memory effect of wood; characterization of wood shape memory effect; frozen strains; topological structure.*

INTRODUCTION

Tendencies in the creation of new materials are based on the results of fundamental and applied research. Development of functional materials the properties of which allow to meet particular purpose is becoming a modern global trend. Wood is a natural multi-functional material with many unique properties, including the dominant feature of smart materials such as shape memory effect. Metal alloys, ceramics and polymers also possess this effect. In wood, the memory effect was experimentally discovered by B.N. Ugolev in the late 1970s (Ugolev 1986). It is based on quasi-residual «frozen» strains, experimentally discovered by B. N. Ugolev in the early 1960s at drying of fastened specimen (Ugolev 1961). In subsequent years, we carried out a systematic study of this phenomenon (Ugolev 2005, 2011, 2014, Gorbacheva 2000, Ugolev et al. 2002, 2011, 2013, Gorbacheva et al. 2014 (1, 2)).

Creation of scientific bases for the development of bio-nanocomposite materials based on wood requires the most possible complete characterization of the shape memory effect. In relation to wood as a highly variable, anisotropic and inhomogeneous material of biological nature this is particularly true. Previously, when testing individual physical and mechanical properties of wood the possible data discrepancy was compensated by a large number of samples. Now it is possible and necessary (due to the expansion of applications of wood and creation of new more sophisticated test

equipment) for each sample to define a set of properties, using modern equipment, not only after testing, but also in-situ.

Modern methods of research allow to conduct qualitative and quantitative assessment of the wood memory effect, to study the nature of the frozen strains, to investigate the changes in the wood structure. The scheme of characterization of wood shape memory effect is presented in Fig.1.

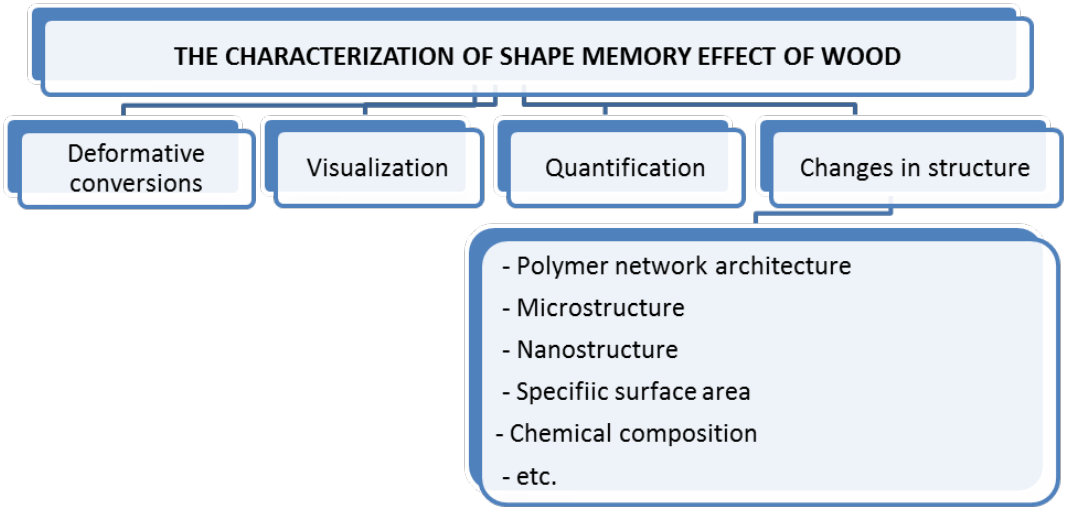

Fig. 1.
The characterization of shape memory effect of wood

OBJECTIVE

The objective of this study is the analysis of methods of characterization of shape memory effect of wood. Experimental research of frozen strains of samples with different deformation prehistories, comparative assessment of the ratio of frozen strains by different techniques were carried out.

MATERIAL, METHOD, EQUIPMENT

For the research of shape memory effect samples of beech and pine sliced veneer along the grain (200x15x0,6mm) were used.

Deformative conversions and visualization

For the description of the deformation conversions the model of hygro(thermo)-mechanical strains of wood (Ugolev 2005,2011,2014), based on the integral law of wood deformation under loading and moisture content and/or temperature changing (Ugolev and Lapshin 1971, Ugolev 1976) is used. This model takes into account the formation of a quasi-residual frozen strains ε_f, besides the known recoverable elastic ε_e and viscous ε_v strains and irreversible plastic strains ε_p.

The frozen strains are the result of temporary reconstruction of wood nanostructure. It takes place under the controlling load influence while wood stiffness increases at drying or cooling (Ugolev 2005, 2014). They disappear at wetting and heating. Study of deformative conversions and visualization were carried out on bent veneer samples by the previously developed method (Ugolev 2011, Ugolev et al. 2013). This method involves determination of all the components of hygro(thermo)-mechanical strains of wood on one sample. Fig. 2 shows the scheme of the shape memory effect of wood. Wood sample has a permanent shape, then it is deformed under certain conditions (programming) and takes a temporary shape. Frozen strains are formed, they are responsible for the shape memory effect of wood. When returning to the initial conditions the disappearance of the frozen strains and recovery of the permanent shape is observed. However, full recovery of the permanent shape doesn't occur due to the irreversible plastic strains, shape after recovery is observed. This method allows to visualize the deformative conversions during the transition from a temporary to a permanent shape, to define the components of hygro(thermo)-mechanical strains.

Frozen strain is equal to the difference between the elastic-viscous strains of the wood at the initial and final temperature and moisture content conditions.

$$\varepsilon_f = \varepsilon_{ev1} - \varepsilon_{ev2} = \frac{\sigma}{E_1} - \frac{\sigma}{E_2} = \sigma\left(\frac{E_2 - E_1}{E_2 \cdot E_1}\right) \quad (1)$$

Additionally, the research of modulus of elasticity in tension along the grain were conducted using the testing machine Instron 3369.

Quantification

For quantitive assesment two important quantities for shape-memory polymers were used (Lendlein and Kelch 2002). Using the model of hygro(thermo)-mechanical strains of wood (Ugolev 2005, Ugolev 2011, Ugolev 2014), equations for the calculation of the shape memory effect quantities Rr and Rf were obtained (Ugolev et al. 2013) (Fig. 2). Consequently, frozen strains are equal to:

$$\varepsilon_f = \varepsilon_{evp}(R_r + R_f - 1) \quad (2)$$

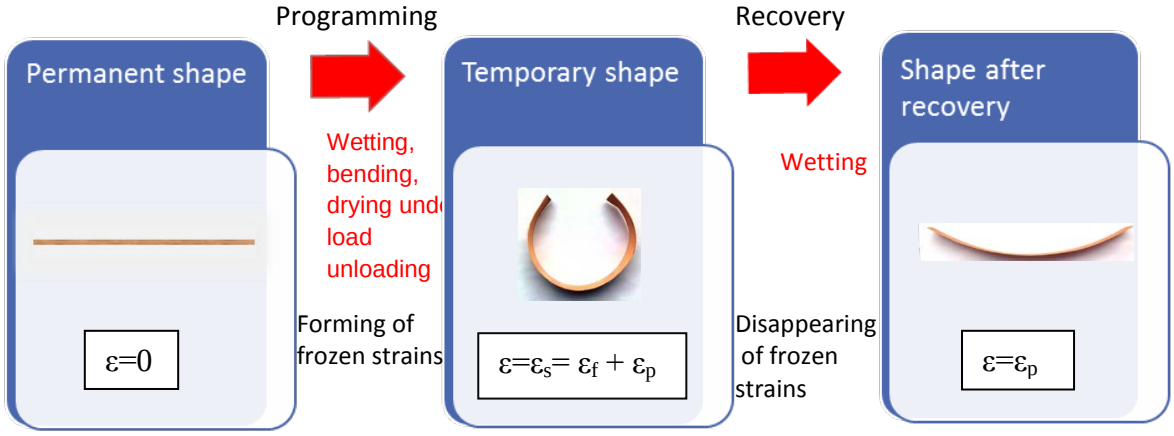

Fig. 2.
The scheme of shape memory effect of wood

Changes in structure

Shape memory effect of wood is explained by reversible changes in wood structure. Wood material can be presented as a composite material consisting of cellulose microfibrils embedded in the lignin-hemicellulose matrix (Erinsh 1977, Salmen 2004). The spatial structure of the matrix is a superposition of three interpenetrating networks: H-net is a network of hydrogen bonds between carbohydrates, and also between lignin and carbohydrates; LH-net is a network with covalent bonds between lignin and hemicelluloses; L-net is a physical one between lignin macromolecules (Erinsh 1977).

Previously, we have conducted experimental studies of memory effect at temperature and moisture content changing on birch wood (Gorbacheva 2000, Ugolev et al. 2002). Based on data from L. Salmen (Salmen 2004), we have suggested that the most remarkable changes occur in the lignin-hemicellulose matrix and in amorphous areas of cellulose. In our subsequent research in cooperation with ISSP of RAS (Ugolev et al. 2007) by method of FTIR spectroscopy it was shown that the drying of the loaded wood birch led to changes primarily in the amorphous areas of cellulose, as well as in the network of hydrogen bonds. In research (Jakes et al. 2012) authors propose that hemicelluloses dominate shape fixity mechanism (Rf) and lignin dominates shape recovery (Rr).

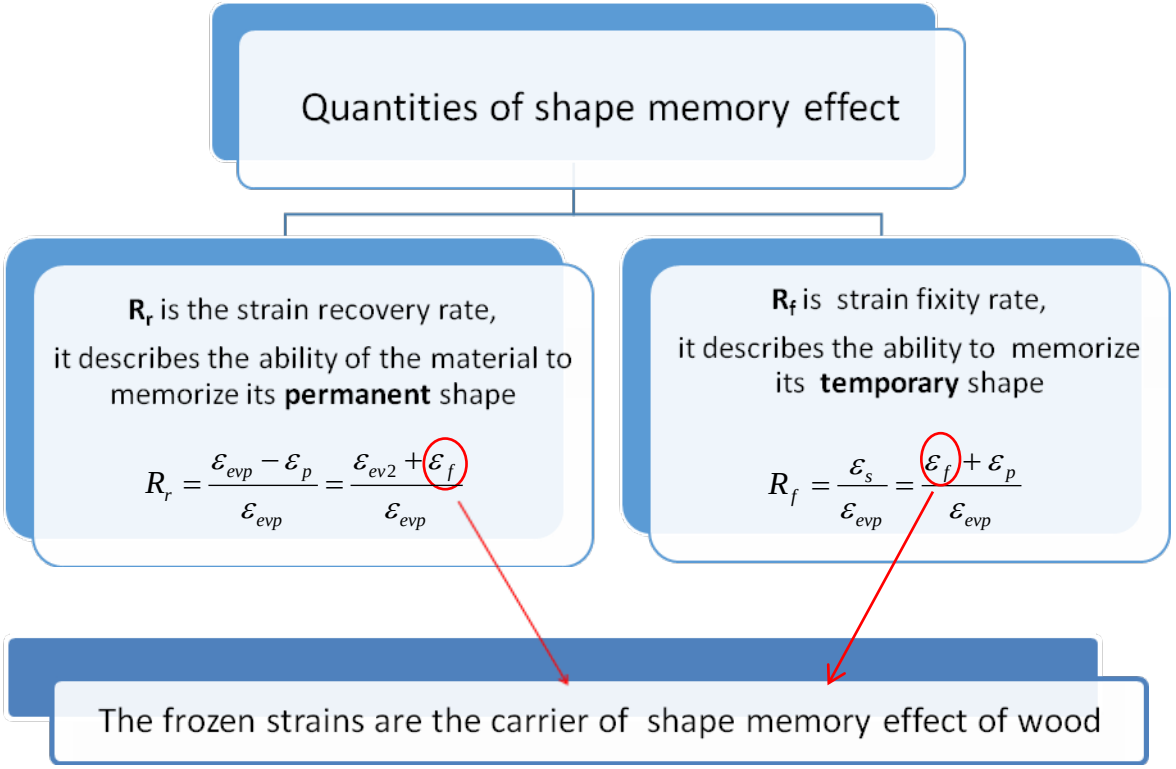

Fig. 3.
The quantities of shape memory effect

For polymers with shape memory it was shown (Sisson and Lendlein 2012) that polymer network architecture forms the basis of this effect. Covalent networks or physical networks trigger switching in the material the transition from the temporary to the permanent shape.

Understanding of the physical networks as formed due to the labile intermolecular bonds of different nature, is one of the fundamental concepts of physics and chemistry of polymers. It underlies the description of deformation processes, crystallization and glass transition polymers etc. Intermolecular interactions simulate physical junctions as formations similar to chemical crosslinking, but having such a low fracture energy that they can break down and re-form as a result of thermal motion. The average concentration of such junctions, unlike chemicals, may change in the process of deformation of the sample.

The special attention is focused on the nature of junction (microcrystalline, another microphase formation, a cluster of chain fragments etc.), its functionality, thermodynamic and kinetic regularities of the formation of the physical networks junctions.

In the implementation of the intermolecular interactions quite strong donor-acceptor bonds, in particular, hydrogen bonds, play a special role. Hydrogen bonds are the most important factor responsible for the rheological properties.

The two-level physical network model (Irzhak et al. 1997) for the description of the nature of intermolecular interaction and interchain organization of polymers in the high-elasticity state can be used for the description of changes at shape memory effect of wood.

Method of the thermomechanical spectrometry (TMS) (Ol'hov et al. 1992, Ol'khov et al. 1996, Ol'khov and Irzhak 1998, Olkhov and Jurkowski 2005), developed at the Institute of chemical physics of the RAS allows to carry out complex research of molecular-topological structure of wood (Bazarnova et al. 2002), detects the changes in physical networks at shape memory effect. In collaboration with Institute of problems of chemical physics of the RAS thermomechanical curves of beech and pine wood were obtained (Gorbacheva et al. 2014 (1, 2)), relaxation parameters, phase state and molecular characteristics of the fragments in the structure of macromolecules topological blocks of wood were determined at shape memory effect.

RESULTS AND DISCUSSION

The comparative assessment of the ratio of frozen strains according to the results of experimental research was carried out. Table 1 shows the results of experimental studies of deformative conversions, quantities of shape memory effect Rr and Rf. The published data about the chemical composition of beech and pine wood are presented in the Table 2. As it follows from Table 1 for beech and pine, the strain fixity rate (Rf) has quite similar values, despite the difference in the chemical composition and structure. This fact is explained by two- component composition of the Rf, and similar values of the modulus of elasticity.

Table 1

Characteristics of shape memory effect of wood

Indicator	Beech	Pine	References
Quantities of shape memory effect of wood			
Rr	0,893	0,785	Experimental data
Rf	0,983	0,99	Experimental data
Deformative conversions			
Modulus of elasticity in tension, GPa	10,4	9,8	Experimental data
Ratio of frozen strains, %	0, 876	0,775	Experimental data
Modulus of elasticity in bending , GPa	12,4	12,2	Borovikov and Ugolev 1989

Table 2

Chemical composition of beech and pine wood

	Beech	Pine	References
Chemical composition , %			
Cellulose	45,4	41,9	Molnar and Bariska 2006
	33,7-46,4	39,7-57,1	Wagenfuhr and Scheiber 1989
	46	53,8	Nikitin 1962
Hemicelluloses	22,2	21,5	Molnar and Bariska 2006
	17,8-25,5	7,9-11,2	Wagenfuhr and Scheiber 1989
	36,9	20,5	Nikitin 1962
Lignin	22,7	29,5	Molnar and Bariska 2006
	11,6-22,7	25,4-29,4	Wagenfuhr and Scheiber 1989
	20,8	26,9-28,2	Nikitin 1962

Original beech and pine wood have topologically diblock amorphous-cluster structure of the pseudonetwork structure, the ratios of blocks are shown on Fig. 4. As a result of bending and consequent drying under load (programming) the samples remember the temporary shape, frozen strains are formed. There is a significant transformation of topological structure, it becomes a multi-block. In beech wood high-temperature amorphous block of pseudonetwork structure with T'c = 19ºC (molecular-mass characteristics M'cn = 2790, M'cw = 4640, K = 1,66) is formed, it becomes triblock.

In pine wood tetrablock stucture is formed. The high-temperature amorphous block of pseudonetwork structure with T'c = 17ºC (molecular-mass characteristics M'cn = 5700, M'cw = 9280, K = 1,63) and crystalline block of pseudo-network branching (with Tm = 0ºC, Mcr = 5000) appear. The changes in the block ratio of the topological structure are shown in Fig. 4.

In the amorphous blocks of both wood species the molecular masses are significantly reduced that indicates the destruction of the three-dimensional networks formed of lignin and hemicelluloses, lignin-carbohydrate and hydrogen bonds.

In the cluster block of beech wood temperature of the beginning of segmental relaxation in a cluster rises, molecular mass of clustered chains almost doubles. The portion of more ordered cluster block decreases for pine wood, for beech wood it increases.

Transition at 19 and 17°C, determined by the TMS for beech and pine wood, can be explained by fluctuations in the liberated OH groups after breaking of hydrogen bonds in the components of wood (Goring 1963).

At returning to the initial conditions, the frozen strains disappeared and the permanent shape is recovered. However, shape after recovery differs from initial form because of irreversible plastic strains (Fig. 2). Initial diblock structure of pine and beech wood with some quantitative changes of molecular relaxation characteristics is restored. Complete structural degradation of the high-temperature amorphous block of pseudonetwork structure and crystalline block of pseudo-network branching takes place. For beech wood the portion of the amorphous block increases, for pine wood previos ratio restores. The geometrical free volume Vf decreases for both species. In the cluster block of beech wood considerable decrease in molecular mass of the cluster fragments of chains is noted, at the increasing of temperature of the beginning of a segmental relaxation in a cluster Tcl, and temperatures of molecular flow Tf.

Method TMS allows to determine the ratio of elastic active chains involved in the formation of the frozen strains. The formation of the high-temperature amorphous block of pseudonetwork structure and crystalline block of pseudo-network branching occurs because of changes in the amorphous block of pseudo-network structure and cluster block of pseudo-network branching. The ratio of frozen strains and blocks involved in their formation is shown in Fig. 4 (by red colour). As can be seen, the portion of frozen strains determined by the SME quantities (Table 1) and by TMS method are almost the same. For pine wood the value of Rf , which is responsible for the formation of a temporary shape, more than for beech, that can be explained by formation of crystalline block of pseudo-network branching.

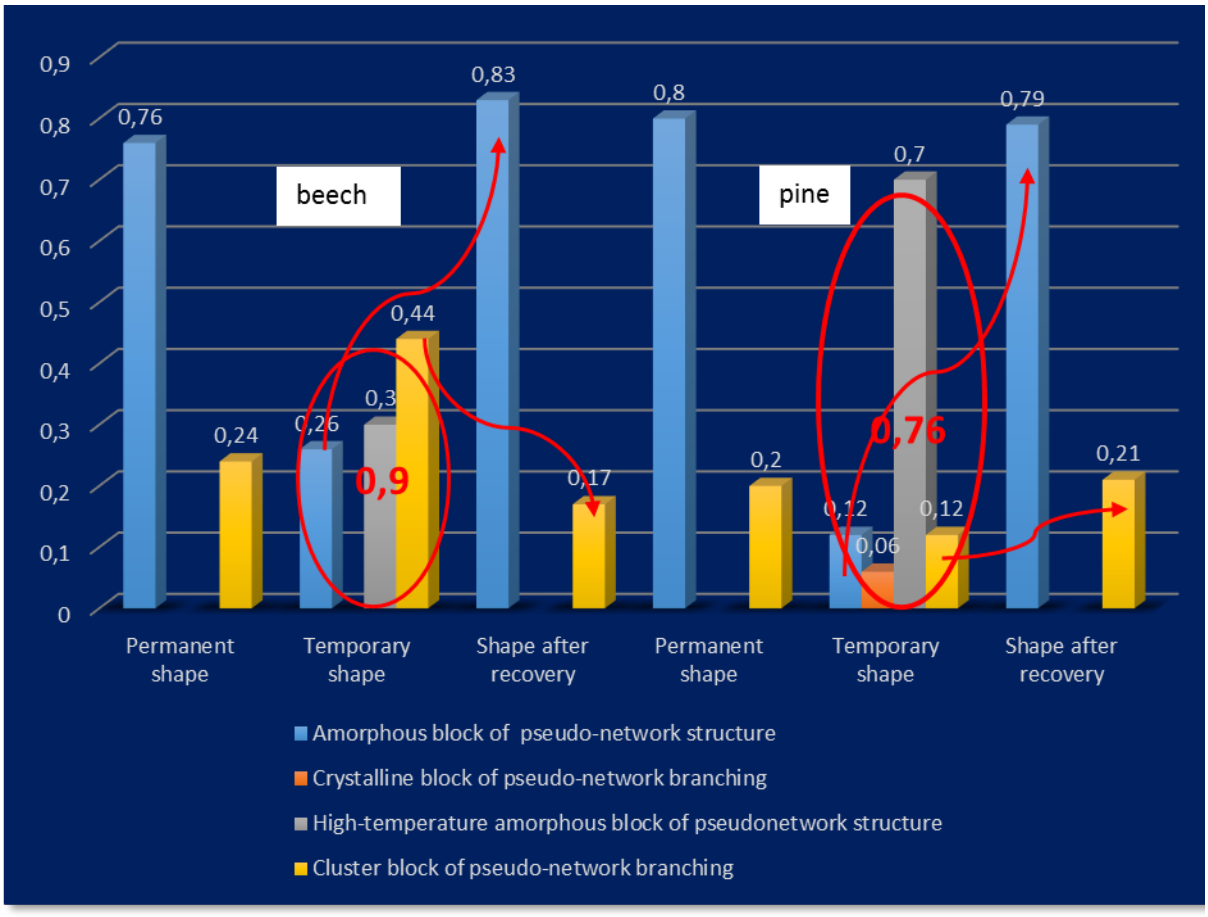

Fig. 4.
Changing of topological structure of beech and pine wood at shape memory effect

CONCLUSIONS

Thus, different methods of characterization of shape memory allow to conduct qualitative and quantitative assessment of the wood memory effect, to study the nature of frozen strains, changes in wood structure. The list of possible methods of characterization of this phenomenon can be expanded. Wood is able to convert molecular-level stimuli-responsiveness into movement on the macroscopic level. Reversible shape changes, typical active movement phenomena are explained by the

transformation of molecular-topological structure of wood. Results of this research belong to the area of fundamental wood science. They can be used for the developing of new multifunctional materials based on wood with a set of specified properties, for the improvement of existing technologies.

ACKNOWLEDGEMENT

This paper is supported by the Federal Program «Research and development on priority directions of development of scientific-technological complex of Russia for 2014-2020", No. 11-65, «Theoretical bases of creation of new nano-, bio - and composite materials on the basis of integrated and sustainable use of forest resources», financed by the Ministry of Education and Science of the Russian Federation. The study was performed at the Center for collective use of scientific equipment «Centre for physical and mechanical tests of wood» on the basis of the scientific and educational center «Nanotechnology in the forest sector» of Moscow State Forest University.

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