Shape memory effect of mycologically destroyed wood

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Abstract. Wood is a natural smart material which possesses shape memory effect (SME). The paper deals with SME behaviour of sound and mycologically destroyed wood and shows the influence of cellulose, hemicelluloses, and lignin content on the wood ability to remember the temporary and to recover the permanent shapes. The research was carried out on sliced veneer samples (beech Fagus sylvatica L. and pine Pinus sylvestris L.) and rotten samples (pocket rot, brown rot) to reveal the influence of on the deformative conversions and quantities of SME. Results of research are shown that at moisture drop the higher values of strain fixity rate for all wood species and types of rot are noted (0.82 – 0.97). The more remarkable difference for sound and rotten wood is observed for strain recovery rate at temperature change. Despite the change of chemical composition for pocket rot the speed of recovery of permanent shape was almost the same as for sound wood. Results of this research can be used for the developing of new biocomposite materials based on wood.

1. Introduction

Wood is a complex of polymers and is a natural smart material [1] being able to perform a self-controlled «intelligent» action and capable of «thinking» like a living organism, adopting and implementing the solution [2,3]. The dominant feature of smart materials is «shape-memory effect» (SME). The last decade is characterized by intense researches in the field of forming of artificial smart materials as polymers with shape memory effect. Alloys, ceramics and polymers with shape memory effect belong to smart materials [4-6]. They are capable to keep the temporary shape received as a result of deformation under certain conditions (programming). Returning to initial physical conditions the sample remembers a permanent shape, i.e. there is a recovery of an original shape. Thus, the sample remembers two forms – permanent and temporary. Some polymers remember three forms [5] whereas the others can remember four ones [7].

The memory effect of wood was experimentally discovered at the end of the 1970s by Prof. B. Ugolev [1]. Further SME’s deformative conversions, visualization and structure was researched by our team [1-3, 8]. Wood material can be presented as a composite material consisting of cellulose microfibrils embedded in the lignin-hemicellulose matrix [9,10]. In our research conducted in collaboration with the Institute of Solid State Physics of the Russian Academy of Sciences [11] by FTIR-spectroscopy method showed that drying of the loaded birch wood led to changes in amorphous areas of cellulose and in network of hydrogen bonds of wood. For polymers with shape memory it was shown [6] that polymer network architecture formed the basis of this effect. Covalent networks or physical networks trigger switching in the material at the transition from the temporary to the permanent shape. Method of the thermomechanical spectrometry (TMS) [12,13] allows carrying out...
complex research of molecular-topological structure of wood, detects the changes in physical networks at SME. The transformation of molecular-topological structure of wood at SME was observed for beech and pine wood [14]. At the moisture-induced shape memory effect the reversibility of the changes in the wood structure at the atomic scale after recovery of the permanent shape was shown in research of K. Kulasiński [15]. In research [16] shape memory effect at twist of pine wood microsample with RH changes was investigated. To clarify the mechanism of the memory effect the experiments by nanoindentation were carried out. Authors propose that hemicelluloses dominate shape fixity mechanism ($R_f$) and lignin dominates shape recovery ($R_r$).

SME is evident for the components of the cell wall of wood also. In research Li et al [17] lignin-copolymers with elastomeric properties were successfully developed using a long alkyl chain (C$_{12}$) hyperbranched prepoly (ester-amine-amide) in a one-pot two-step bulk polycondensation reaction. The lignin copolymer elastomers with 30% lignin content showed optimal mechanical properties and good thermal-stimulated SME behaviors.

Thus, further studies are needed in this area to clarify the role of cell wall components on the SME behavior. Since the rot leads to change in component composition of wood without additional chemical reagents the mycologically destroyed wood samples are good objects for research of the influence of change in chemical composition on the SME quantities.

Experimental studies carried out on rotten samples allows to reveal the influence of the content of cellulose, hemicelluloses and lignin on the deformative conversions and SME quantities. Brown rot fungi are the most prevalent with regard to attack on coniferous, structural wood products. The wood decayed by brown rot fungi is typically brown and crumbly and it is degraded via both non-enzymatic and enzymatic systems. A series of cellulolytic enzymes are employed in the degradation process by brown rot fungi, but no lignin degrading enzymes are typically involved.

White rot fungi are typically associated with hardwood decay and their wood decay patterns can take on different forms. White rotten wood normally has a bleached appearance, and this may either occur uniformly, leaving the wood as a spongy or stringy mass, or it may appear as a selective decay or a pocket rot. White rot fungi possess both cellulolytic and lignin degrading enzymes [18].

The aim of this study is a comparative analysis of the SME behaviour of sound and mycologically destroyed wood.

2. Materials and methods

The samples of sliced veneer of beech (Fagus sylvatica L.) and pine (Pinus sylvestris L.) sound wood taken from Woodstock Co. (Khimki city, Russian Federation) were used in the work. We used 20 specimens with sizes of 90x2x2 mm (L×T×R). The samples of mycologically destroyed wood with white rot (pocket rot, PR) and brown rot (BR) of the same sizes were tested. The temperature (t) of samples was varied in the range of 2-100ºC, moisture content (W) of samples was of 0 - 150%. Studies of deformative conversions and visualization at shape memory effect were carried out at bending by means of the determination of all the components of hygro(thermo)-mechanical strains of wood on one sample and allows visualizing the deformative conversions during the transition from a temporary to a permanent shape [1-3, 19]. The visualization was carried out by digital camera Nikon COOLPIX P520 (Nikon,China) during the experiment for 50 min for every specimen. The storyboard and timing of the process of recovering of the permanent shape for all samples at wetting or heating were carried out. Moisture content of samples W was determined by weight method. The value of each strain component was estimated using the equation of the bending axis of the rod and well-known geometry relations using the images after visualization of SME, AutoCAD was used for measurements of changes of specimen shapes.

The experiments of SME behavior at temperature change were carried out at moisture content W ≥ 30% in order to eliminate the influence of shrinkage and swelling on value of strains. Research of the SME at temperature change was conducted according to the following method. The loading of sample (bending) was done at moisture content W ≥ 30% and the temperature of 100°C, exposure during 10 min. Then in the sample thermomechanical strain ($\varepsilon_{\text{th}}$) was measured. Then the samples were cooled
under load to $t=2^\circ C$ and exposed during 10 min prior to measurement of thermomechanical strain $\varepsilon_{evp}$, it remained constant due to forming of frozen strains. After unloading of sample and exposure of 10 min, elastic-viscous strain of cooled sample ($\varepsilon_{ev2}$) was measured. Heated to temperature of 100 $^\circ C$ and exposed during 10 min at 100 $^\circ C$ followed by the determination of the frozen strain ($\varepsilon_{f}$) and plastic strain ($\varepsilon_{p}$).

SME was also researched under moisture content change. The experiment was carried along the grain to minimize the influence of shrinkage and swelling on value of strains. We loaded the sample at moisture content $W_i \geq 30\%$, at 80 $^\circ C$ during 10 min and then measured the hygromechanical strain ($\varepsilon_{evp}$). Then the sample was dried up to moisture of 8% at 80$^\circ C$ under load and we estimated $\varepsilon_{evp}$ again. After unloading and exposure 10 min elastic-viscous strain of dried sample ($\varepsilon_{ev2}$) was determined. Finally, we wet the sample up to the initial moisture $\geq 30\%$ at 80$^\circ C$ and determined frozen strain ($\varepsilon_{f}$) and plastic strain ($\varepsilon_{p}$).

The obtained parameters were used to calculate the strain recovery rate $R_r$, describing the ability of the material to memorize its permanent shape and strain fixity rate ($R_f$) [5] showing the ability to fix the mechanical deformation by the formula (1) and (2) [2,3], respectively:

$$R_r = \frac{\varepsilon_{evp} - \varepsilon_p}{\varepsilon_{evp}}, \quad (1)$$

$$R_f = \frac{\varepsilon_s}{\varepsilon_{evp}} = \frac{\varepsilon_f + \varepsilon_p}{\varepsilon_{evp}}, \quad (2)$$

where, $\varepsilon_{evp}$ is the total hygro(thermo)-mechanical strain, $\varepsilon_p$ is irreversible, plastic strain,

Samples were marked with alphanumeric marking, where the characters indicated the type of rot or wood species (BR – brown rot, PR – pocket rot, B – beech, P – pine), the first number indicated the type of SME research (1 – at temperature change, 2 – at moisture content change) the second number was the serial number of the sample, for example, BR-2-1 meant the specimen of brown rot (#1) was researched of SME at moisture content change.

For preliminary study of cellulose content was determined by the method of Kurschner-Hoffer, lignin by the method of Popov [21]. Published results of studies of the chemical composition is often difficult to compare due to different methods of determination of components of wood substance, natural variability of wood, in addition decay stage also affects [20-22].

3. Results and discussion

The results of determination of thermomechanical and hygromechanical strains are presented in figure 1 and figure 2. As an example, the components of strains ($\varepsilon_{evp}$, $\varepsilon_s$, $\varepsilon_{ev2}$, $\varepsilon_p$) are shown for specimens of brown (BR-2-1) and pocket (PR-1-1) rot. The strain components for sound and mycologically destroyed wood are similar with different quantitative relations (figures 1,2). The values of plastic strain are slightly dependent on the wood species and type of decay, especially for the case of hygromechanical strains, for example, for samples BR-2-1, PR-2-1, P-2-2, B-2-2. The results of the determination of the components of the thermomechanical strains showed that maximum ratios of set and plastic strains were found for the samples of pocket rot (0.63 and 0.27, respectively (figure 1, sample PR-1-2). For samples of brown and pocket rot the ratios of set strains were varied in the range of 0.47 to 0.87 (figure 1 and 2, samples BR-1-1, PR-1-1, PR-1-2, PR-1-3 and BR-2-1, PR-2-1). Chemical composition of sound and rotten wood is presented in table 1. The decrease of lignin content for pocket rot and increase of lignin content for brown rot were observed in researches and explained by selective action of fungi on components of wood cell wall.
For moisture content change the ratios of plastic strains decreased: 0.09 - 0.26 and 0.07 - 0.14 for pocket and brown rot, respectively (figure 1 and 2, samples PR-1-3 and BR-2-1). Wood species and rot type have a greater impact on the ratio of components of thermomechanical strains than for hygromechanical ones.

Since frozen strains are the carrier of SME, high values of $R_f$ can be predicted. The strain fixity rates $R_f$ for sound and rotten wood at temperature (figure 5) and moisture content change (figure 6) were obtained using the components of strains (figures 1,2). At moisture content change for all wood species and rot types the high values of $R_f$ were noted (0.82 – 0.97), these values were quite close to...
the obtained values for sound wood, particularly (figure 6, samples PR-2-2, BR-2-1. This is explained by two-component character of set strain which determines the value of $R_f$. Set strain includes the frozen and plastic strains. At temperature changes the more remarkable difference for sound and rotten wood was observed. The values of the $R_f$ at the temperature change were in range 0.39 - 0.82, for the samples of brown and pocket rot, respectively (figure 5). Values of $R_f$ for pocket rot were higher (sample PR-1-1 (figure 5), sample (PR-2-figure 6)), due to corrosion type of decay.

![Figure 5. Strain fixity rate ($R_f$) at temperature change.](image)

![Figure 6. Strain recovery rate ($R_r$) at moisture content change.](image)

The strain recovery rates $R_r$ value for sound and rotten wood at temperature and moisture content changes accordingly to above mentioned methods, in ranges 100-2 C and >30-8 %, respectively, are presented in figures 7 and 8. The values of elastic-viscous and frozen strains affect the value of $R_r$ which reflects the ability of wood to memorize temporary shape. The strain recovery rate $R_r$ for mycologically destroyed wood was slightly higher than the sound wood (figure 7 and 8). The $R_r$ at temperature change from 100 to 2 C for rotten wood was slightly higher (figure 7, samples PR-1-4, BR-1-2) than for sound wood (figure 7, samples P-1-1, B-1-1), despite the decrease in the lignin content for the sample of pocket rot and the increase of the content for brown rot (table 1). Thus, the values of $R_r$ are more sensitive to the changes of the wood chemical composition.

![Figure 7. Strain recovery rate ($R_r$) at temperature change (100-2 C).](image)

![Figure 8. Strain recovery rate ($R_r$) at moisture content change (>30-8 %).](image)

In figure 9 the storyboard and timing of the process of recovering of the permanent shape of the sound (beech) and rotten wood (pocket rot) samples at wetting are shown.

The samples during the recovery of permanent shape demonstrated the behavior of actively moving material [6]. Wood is able to convert molecular-level stimuli-responsiveness into movement on the macroscopic level. The recovery process was very fast, the sample of pocket rot restored its shape within 43 s as presented in figure 9. Despite the decrease of the lignin content (table 1) the strain recovery rate $R_r$ of pocket rot sample was higher than for sound beech wood (figure 9). It confirms the correctness of the model of hygro(thermo)-mechanical strains of wood and results of SME investigation by method of TMS [3,14].
4. Conclusion

The values of the components of hygro- and thermomechanical strains and SME quantities for sound and mycologically destroyed wood were obtained. Wood species and rot type have a greater impact on the ratio of components of thermomechanical strains than for hygromechanical ones. Despite the significant changes in the chemical composition, a decrease of the lignin content for pocket rot and a decrease of the cellulose content for brown rot led to a slight change in the ratios of components of the hygromechanical strains. The decrease of the content of hemicelluloses and lignin for the samples of brown and pocket rot practically did not affect the ratio of the thermomechanical strain components. Frozen strains are the carrier of SME, at moisture content change significant frozen strains were observed for mycologically destroyed wood (0.49-0.73 for pocket rot and 0.54 - 0.78 for brown rot). For rotten wood the ratios of frozen strain were higher than for sound wood.

At moisture content change for all wood species and rot types the high values of $R_f$ were noted (0.82 – 0.97), these values were quite close to the obtained values for sound wood. At temperature change from 100 to 2°C the more remarkable difference for sound and rotten wood was observed.

The strain recovery rate $R_r$ for mycologically destroyed wood were slightly higher than the sound wood. The $R_r$ at temperature changes for mycologically destroyed wood was slightly higher than for native wood (0.73-0.76), despite the decrease of the lignin content for the pocket rot sample and the increase of the content for brown rot. Thus, the values of $R_r$ are more sensitive to the changes of the wood chemical composition.

The samples of pocket rot during the recovery of permanent shape demonstrated the behavior of actively moving material. Despite the decrease of the content of lignin the strain recovery rate $R_r$ of pocket rot sample was higher than for sound wood.

The experiments confirmed the correctness of the model of hygro(thermo)-mechanical strains of wood. Further investigation of SME of mycologically destroyed wood by method of TMS is necessary. Results of this research belong to the area of fundamental wood science and can be used for the developing of new smart materials based on wood and for the improvement of existing technologies.

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