POLİTEKNİK DERGİSİ

JOURNAL of POLYTECHNIC

ISSN: 1302-0900 (PRINT), ISSN: 2147-9429 (ONLINE)
URL: http://dergipark.gov.tr/politeknik

Wood property improvement of siberian pine by combination of boric acid impregnation and in-situ polymerization of Ɛ-caprolactone

***Yazar(lar)(Author(s))**: Mahmut Ali ERMEYDAN[1], Eylem DİZMAN TOMAK[2], Zeynep NurKARTAL[3]*

ORCID[1]: 0000-0001-6389-2649

ORCID[2]: 0000-0001-8654-0005

ORCID[3]: 0000-0002-4696-242X

Bu makaleye şu şekilde atıfta bulunabilirsiniz(To cite to this article): Ermeydan M. A., Tomak E. D. ve Kartal Z. N., "Wood property improvement of siberian pine by combination of boric acid impregnation and in-situ polymerization of ε-caprolactone", ***Politeknik Dergisi***, 22(1): 157-161, (2019).

Erişim linki (To link to this article): http://dergipark.gov.tr/politeknik/archive

DOI: 10.2339/politeknik.386966

Wood Property Improvement of Siberian Pine by Combination of Boric Acid Impregnation and *In-Situ* Polymerization of Ɛ-Caprolactone

Araştırma Makalesi / Research Article

Mahmut Ali ERMEYDAN*, Eylem DİZMAN TOMAK, Zeynep Nur KARTAL
Forest Industry Engineering Department, Faculty of Forestry, Bursa Technical University, Turkey

(Geliş /Received : 14.11.2017 ; Kabul /Accepted : 07.12.2017)

ABSTRACT

Wood is an excellent engineering material with its light weight and high mechanical properties. However, it is susceptible to biodegradation due to its hygroscopic nature and chemical composition that limits both its indoor and outdoor usage. Boron compounds which are known as eco-friendly wood preservatives have limited utility at outdoor conditions since they are easily leached out from wood by water. The aim of this study is to prevent boron leaching by creating a polymer network that encapsulates boron compound inside the wood cell walls, thus decay resistance, dimensional stability and water repellence are improved. In the study, Siberian pine samples were impregnated with 1% boric acid in DMF(N,N-Dimethylformamide) and further ε-caprolactone monomer (1% SnOct2 as initiator) mixture for further in-situ polymerization were carried out in the oven at 150°C for 3 hours. Prior to decay testing, leaching test was conducted in order to evaluate any loss in effectiveness in decay resistance against to C. puteana and C. versicolor attack due to possibility of boron leaching from wood. The results showed that leached samples had lower weight loss than unleached samples after C. puteana attack, however, the weight loss by C. versicolor attack increased in leached samples. Decay resistance of treated samples was found to be 7-99% in comparison with references. Boric acid and polymer combination increased dimensional stability (25% ASE), and water repellence (15%) of wood compared to references without deformation. This method showed that curing may be an alternative for wood modification with in-situ polycaprolactone polymerization in order to use hazardous solvent media for polymerization.

Keywords: Poly(ε-caprolactone), wood modification, dimensional stability, decay resistance.

1. INTRODUCTION

Outdoor utilization of wood has natural limits due to the low durability of most wood species against biological organisms. Wood density, mechanical strength and aesthetic appearance change and reduce because of fungal growth in wood. Therefore, wood preservatives are used to protect wood products from fungal attack, thus service-life of the products may be increased [1]. As mentioned above several chemicals or methods have been used so far to protect wood partially, e.g. surface, or total timber can be treated to eliminate biological degradation. Heat treatment, impregnation of wood preservatives and chemical modification are some of the wood conservation methods. The old and most common methods are impregnation of some toxic chemicals like copper, cobalt, zinc or arsenic into the wood structure due to their effectiveness and price. Even though most of those chemicals are very effective against biodegradation; there is a huge environmental concern due to the utilization of those toxic preservatives. Besides, for the last decades, people start to research and apply an alternative method for wood protection. One of those methods is chemical modification of wood. Chemical modifications both improve durability of wood without the use of conventional biocides, and other wood properties such as dimensional stability and water repellence. There are even commercial methods have been already established to chemically modify wood. Acetylation, furfurylation and dimethylol dihydroxy ethylene urea (DMDHEU) modification are some modification methods [2]. There are still several investigations are carried out to find more effective and cheaper modification methods.

Boron compounds as a wood protection agent are known to be an active fire retardant and effective against both insect and fungi attacks [3]. Effects of boron compounds on mechanical, biological and dimensional stability of wood and wood products have already been investigated in detail [4]. In addition, it is well known that boron compounds can be leached out when used for outdoor purposes, thus wood products become vulnerable to biological organisms [5]. To overcome this problem researchers have studied to keep boron compounds into the wood cell wall and tried to fix it inside [4-8]. In those studies, the general purpose was in-situ polymerization of various polymers to fix boron compounds into the cell walls.

Contrary to conventional hydrophobic polymers like styrene/acrylates, Ɛ-caprolactone can enter and be polymerized inside the wood cell walls. Recently, hydrophobic Ɛ-caprolactone monomer was successfully achieved to graft into the wood cell walls and introduced as a successful novel modification method [9] which

---

* *Soumlu azar (Corresponding Author)*
e-mail : mahmut.ermeydan@btu.edu.tr

increase hydrophobicity (35%) and dimensional stability (40%) of wood. Ɛ-caprolactone can be grafted from the –OH groups of the cell wall polymers to form hydrophobic polycaprolactone polymer. In this study, Siberian pine samples were modified with a combination of boric acid impregnation and further polycaprolactone grafting in wood to reduce boric acid leaching from wood cell walls by blocking wood cell cavities by polymer, thus we aim to get better fungal resistance in the long term and outdoor usage of wood. It is thought that boron compounds may be trapped inside wood cell walls by polycaprolactone modification and this may have a potential to limit boron leaching. Modified wood has improved water absorption and dimensional stability properties, and thus we found that curing even at high temperature may be an alternative to polymerize Ɛ-caprolactone (CL) in order to use solvent-based modification.

2. MATERIAL and METHOD

Bu çalışmada, düz tip yutucu plakalı (Model I) ve düz Wood material: Siberian pine sapwood samples with dimensions of 15 mm (radial) x 5 mm (tangential) x 30 mm (longitudinal) were supplied from Osmanlı Mobilya, Bursa, Turkey.

Chemicals: Boric acid (BA), epsilon-caprolactone (CL), tin(II) 2-ethylhexanoate (TEH), dimethyl formamide (DMF) were ordered from Sigma and used as delivered. Malt extract-agar and sterile plastic petri dishes (90 mm diameter) were used for decay test. Distilled water was used for all necessary cases.

Modification of Wood: The Ɛ-caprolacton polymerization in wood was applied as reported before with some modifications [9]. Wood samples were soaked in DMF over night to swell wood structure. This step was applied for better chemical uptake into the cell walls in the further steps. DMF was poured out and later on, 1% boric acid (BA) was dissolved in DMF, than poured onto already swelled wood and BA was impregnated in wood cell walls 30 minutes under vacuum. Than BA solution were decanted from the samples. Same amount of CL monomer, DMF and 1% TEH as catalyst were mixed together and poured onto samples, again 30 minutes of vacuum were applied for better uptake monomer by wood cell walls and waited overnight for better impregnation. Than the monomer solution were removed and samples were covered with aluminum foil. Polymerization reaction was started by heating samples in a sealed oven at 150°C. After reaction for 3 hours, wood samples were washed half an hour with acetone which is a good solvent for polycaprolactone, then washed with distillated water for four hours. In Figure 1, impregnation steps were explained. 25 replicate samples were used.

Weight Percentage Gain (WPG) and Volume Change: Weight and volume changes caused by the chemical treatments were measured before and after each treatment (Ɛ-caprolactone polymerization, water immersion, and oven drying).

Water Uptake (WU), Mass Loss, Swelling Coefficient (S), and Anti-Swelling Efficiency (ASE): The reference and modified wood samples were soaked into distillated water for five days with a fair shaking (Soaking cycle 1). Then samples were dried into an oven at 103°C over night (Drying cycle 1). Samples were soaked again into distilled water for the second water-soaking and drying cycles. The dimensional stability of the modified wood samples was obtained by calculating the S and the ASE values as reported [9, 10]. The equations for swelling, anti-swelling efficiency, and WU calculations are given in [9]. The water repellence ability of modified wood is described by the WU calculations.

Leaching Test: Leaching test was performed to treated samples according to EN 84 standard in order to evaluate any loss in effectiveness in biological resistance for 14 days.

Decay Resistance Test: Decay test was performed according to principles of EN 113, with some modifications on sample dimensions, kolle flasks, and total test period. Malt extract agar of 4.8% concentration and samples were sterilized in an autoclave at pressure of about 0.1 MPa at 120°C for 25 minutes. A brown-rot fungus, Coniophora puteana and white rot fungus, Coriolus versicolor was inoculated to sterile malt extract agar medium in the petri dishes. Two samples (treated and untreated) were placed on the growing mycelium in each petri dish and then were incubated at 20°C and 65% RH for 8 weeks. At the end of the test, samples were removed from the petri dishes, cleaned, and dried at a temperature of 103°C. Weight loss was calculated on the basis of oven-dry weight before and after decay test.

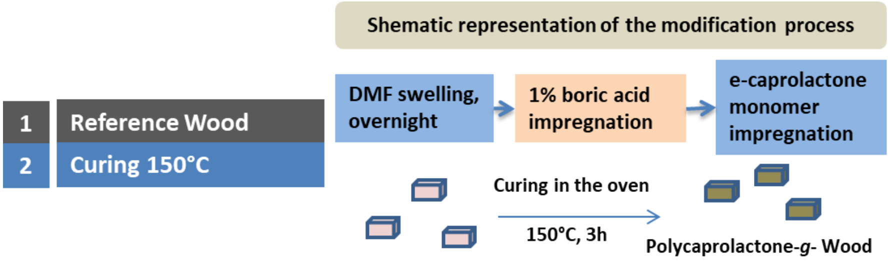


Figure 1. Left: 2 sets of samples, numbering and nomenclatures which were used during the study. Right: Schematic description of Ɛ-caprolactone modification.

3. RESULTS AND DISCUSSION

Physical Changes and Stability: Ɛ-caprolactone polymerization to graft polycaprolactone into wood cell walls is a novel modification method which achieved for the first time insertion of a hydrophobic monomer into the cell walls [9]. Use of DMF as a solvent, one of the critical parameter for a successful wood cell wall modification, because DMF like polar aprotic solvent swells wood structure up to 12-14% [9, 12]. Swelling of wood provides ease to insert molecules into cell wall structure. Success of this process was proved in [9]. This principle was carried out to get better results during impregnation of boric acid as well. On the other hand, we already reported several combinations of BA+CL modification in [13] which introduces different modification sets to find the best method for boric acid and polycaprolactone combination. However, in this study [13], there was no information on dimensional stability and water repellence properties of modified wood. In the current study only one type of modification was studied. BA first impregnated and later CL was polymerized in the oven at high temperature to get better linkage of polymer to cell wall polymers. The method reported in [13] was slightly modified, the modification temperature and the reaction time increased from 2h to 3h to get better WPG%, dimensional stability and durability. Besides, addition to [13], two fungi species were tested in this study. By curing wood samples for 3h in order to make polymerization reaction at 150°C, we aimed to find the optimum reaction time for modification without making any deformation in wood structure. Wood polymers, especially hemicelluloses and lignin, can start to degrade above temperatures above 120°C. Curing is basically oven heating of already impregnated samples which is more practical and environmentally safe than making reactions in organic solvents.

Contrary to [13], we found better WPG% and volume increase%, 9±1,5% and 6,9±1%, respectively (Figure 2). This is probably due to the increased reaction time (2 to 3 hours) and better heating (95 to 150°C). However, as shown in Figure 1, mass loss occurred during water immersion and drying cycles is rather high than reference (9% and 2% respectively). This is probably due to the combination of boric acid and tin (II) 2-ethylhexanoate which increase acidity of the reaction mixture. Thus, increased acidity may spoil cellulose glycosidic bonds and further deform wood structure. Also, some of the homopolymer which cannot be removed from the lumen area during the initial washing steps, may be removed from wood structure.

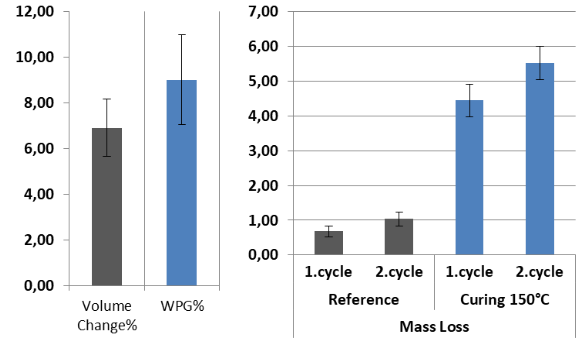
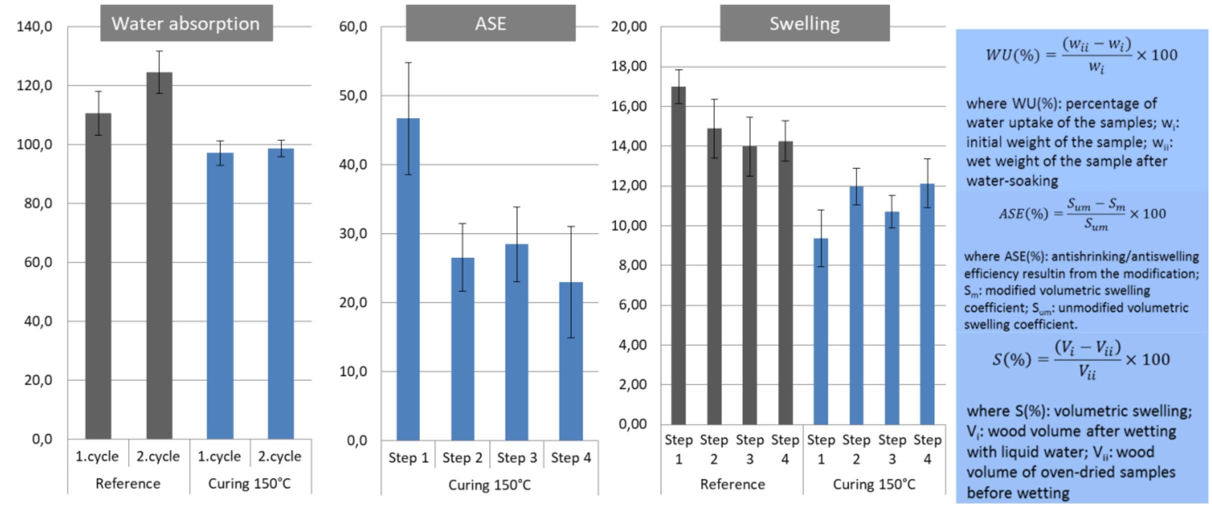


Figure 2. Left: WPG% and volume change% of samples after Ɛ-caprolactone modification. Right: Mass loss of samples during water immersion cycles.

Ɛ-caprolactone modification is known to be an effective method in terms of dimensional stability and water repellence as already reported [9]. Water repellence of cured samples is shown in Figure 3. Water absorption of modified samples reduced about 15% compared to reference wood which proves that there is a certain amount of polymer inside the cell walls. Another important analysis is anti-swelling efficiency calculation which shows dimensional stability of the modified samples. The weight percent gain (WPG%) and volume change (%) shown in Figure 2 already provided a first indication on the success of the modification in terms of dimensional stability. However for a better



$$WU(\%) = \frac{(w_{ii} - w_i)}{w_i} \times 100$$

where WU(%): percentage of water uptake of the samples; w_i: initial weight of the sample; w_{ii}: wet weight of the sample after water-soaking

$$ASE(\%) = \frac{S_{um} - S_m}{S_{um}} \times 100$$

where ASE(%): antishrinking/antiswelling efficiency resultin from the modification; S_m: modified volumetric swelling coefficient; S_{um}: unmodified volumetric swelling coefficient.

$$S(\%) = \frac{(V_i - V_{ii})}{V_{ii}} \times 100$$

where S(%): volumetric swelling; V_i: wood volume after wetting with liquid water; V_{ii}: wood volume of oven-dried samples before wetting

Figure 3. Left: Water absorption of control and modified samples during ASE cycles in 14 days, Middle: ASE values of Right: WPG% and volume change after modification reaction. WU, ASE, S calculations are given in blue boxes on the right.

understanding of dimensional stability, swelling and ASE measurements were carried out. Low swelling values between 10-12% is belong to modified samples as shown in Figure 3, where swelling of the reference is about 14-16% at all water soaking-oven drying cycles. Volumetric S values of modified samples are reduced 25% levels which already show the first indication of better dimensional stability. ASE of the modified samples are calculated for each water immersion and drying step (totally four steps) [9, 10]. As shown in Figure 3, ASE of modified sample became almost stable 25% after first step which means modified sample has better dimensional stability than references.

Decay Resistance of Samples: The results of the decaying test are shown in Figure 4. The unleached and leached test samples exposed to C. puteana attack showed 6.21 and 0.33% weight loss, respectively. In the case of C. versicolor attack, weight loss was found to be 5.56 and 24.18% for unleached and leached test samples, respectively. The weight loss of the references exposed to decay fungi verified the decay test was valid according to EN 113, and the test conditions were suitable for the growth of fungi (Figure 4). As can be seen from the Figure 4, modified test samples exhibited biological resistance against both fungi attack. The biological resistance of unleached and leached test samples in comparison to references was found as 67 and 99% after C. puteana attack and 81 and 7% after C. versicolor attack, respectively. However, the average weight loss of test samples should be less than 3% of their initial dry weight for a suitable decay resistance needed from a potential wood preservative against decay fungi according to EN 113 test. Only one group (leached and exposed to C. puteana attack) exhibited a relatively low weight loss (<0.5) among the test groups, and met the EN 113 criteria. Surprisingly, unleached test samples had greater weight loss than leached samples after C. puteana attack. The probable reason for this finding could be C. puteana might digest the polymer in the lumens of unleached samples. In the leached samples, polymer in the lumens might leach out from wood during the leaching procedure and the amount of retained polymer and tin(II) 2-ethylhexanoate in the cell wall protected wood against C. puteana attack. Possible mechanisms of decay resistance of Ɛ-caprolacton are well explained in our previous study [13].

Organotin compounds are effective against brown-rot fungi [14, 15]. In the case of C. versicolor attack, similar statements could also be possible for unleached samples. Polymer in the lumens might be digested by C. versicolor attack. Opposite to findings in C. puteana degradation, C. versicolor caused a great weight loss in leached samples. Tin(II) 2-ethylhexanoate in the cell wall might be not toxic for C. versicolor. Another reason could be retained tin(II) 2-ethylhexanoate in wood after leaching might not be sufficient level for protection against C. versicolor attack. Both chemical (boron, tin(II) 2-ethylhexanoate and polymer) leaching during the test and weight loss of wood components due to white rot decay itself, could be possible two reasons for higher weight loss in leached samples than unleached samples. White rot fungi have an ability to adsorb and accumulate heavy metals and therefore can be used as bioremediation purposes of contaminated substances. Some fungal melanins are efficient bioabsorbers of copper [15, 16] or toxic tin compounds [15, 17]. T. versicolor was found to be resistant to metals (Cd, Zn, Ni, Co, Cr, Mo, Pb, Hg, and Sn), whereas A. mellea, Lentinus sp., Pholiota nameko, Pleurotus sp., Pycnoporus sanguineus, and S. commune were less resistant [18]. In this study, boric acid supposed to be leached out from wood due to high weight loss of leached samples by C. versicolor. Boric acid is known as a toxic chemical for C. versicolor attacks. If boric acid presented inside wood after leaching, C. versicolor degradation would not be occurred such a high level (weight loss of 24.18%) in wood. Further studies such as boron detection in wood after leaching and Raman spectroscopy are needed to confirm this observation.

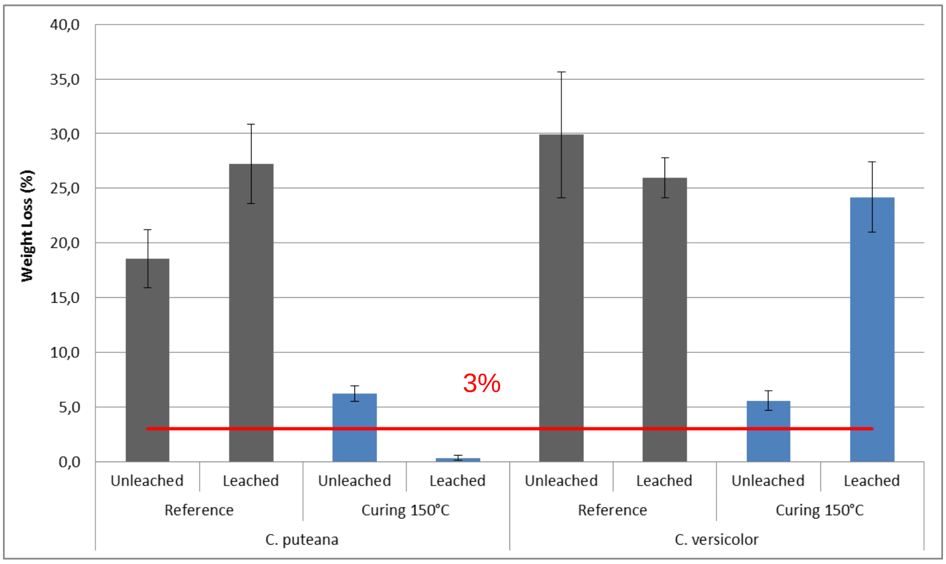


Figure 4. Weight loss (%) of samples after *C. puteana* and *C. versicolor* attack

6. CONCLUSION

In this study, Siberian pine samples were treated with 1% boric acid and Ɛ-caprolactone monomer solution for further polymerization of Ɛ-caprolactone at 150°C in the oven to find out the efficiency of curing modification and boric acid- polycaprolactone method. Modified samples have stable and good dimensional stability in the various immersion cycles and better water repellence than reference. However, probably due to the acidity of the boric acid, wood structure was degenerated and mass loss due to water immersion cycles is still significant. Decay test of the samples showed that the modification is successful against fungi growth in comparison to references. Modified samples exhibited excellent protection against C. puteana after leaching, however, C. versicolor caused a great weight loss in the leached samples. Tin(II) 2-ethylhexanoate in the modification process might play an important role on decay resistance. Boric acid supposed to be leached out from wood during leaching procedure. Further studies are still required to fully unravel mechanism of decay resistance.

ACKNOWLEDGEMENT

This research was supported by the TÜBİTAK research grant (Project No: 116O578). We would like to thank Mert Babacan from BTU, Bursa.

REFERENCES

[1] Hill C. A. S., “***Wood modification : chemical, thermal and other processes***”, John Wiley & Sons, Chichester, England, Hoboken, NJ, (2006).

[2] Rowell R. M., “***Handbook of Wood Chemistry and Wood Composites***”, CRC Press, Boca Raton, FL, (2000).

[3] Kartal S. N., Yoshimura T., Imamura Y., “Decay and termite resistance of boron-treated and chemically modified wood by in situ co-polymerization of allyl glycidyl ether (AGE) with methyl methacrylate (MMA)”, ***International Biodeterioration & Biodegradation***, 53(2): 111-117, (2004).

[4] Yalinkilic M. K., Gezer E. D., Tkahashi M., Demirci Z., Ilhan R., Imamura Y., “Boron addition to non or low-formaldeyde cross-linking reagents to enhance biological resistance and dimensional stability of wood”, ***Holz als Roh- und Werkstoff***, 57: 351-357, (1999).

[5] Dauvergne E. T., Soulounganga P., Gerardin P., Loubinoux B., “Glycerol/glyoxal: a new boron fixation system for wood preservation and dimensional stabilization”, ***Holzforschung***, 54: 123–126, (2000).

[6] Temiz A., Alfredsen G., Eikenes M., Terziev N., "Decay Resistance Of Wood Treated With Boric Acid And Tall Oil Derivates", ***Bioresource Technology***, 99: 2102-2106, (2008).

[7] Kartal S. N., Yoshimura T., Imamura Y., “Modification of wood with Si compounds to limit boron leaching from treated wood and to increase termite and decay resistance”, ***International Biodeterioration & Biodegradation***, 63:187–190, (2009).

[8] Jebrane M. and Heinmaa I., “Covalent fixation of boron in wood through transesterification with vinyl ester of carboxyphenylboronic acid”, ***Holzforschung***, 70(6): 577-583, (2015).

[9] Ermeydan M. A., Cabane E., Hass P., Koetz J., Burgert I., “Fully biodegradable modification of wood for improvement of dimensional stability and water absorption properties by poly(ε-caprolactone) grafting into the cell walls”, ***Green Chemistry***, 16(6): 3313-3321, (2014).

[10] Rowell R. M. and Ellis W. D., “Determination of dimensional stability of wood using the water-soaking method”, ***Wood and Fiber***, 10(2): 104-111, (1978).

[11] Zabel R. A., Morrell J. J., “***Wood Microbiology Decay and Its Prevention***”, Academic Press: San Diego, (1992).

[12] Mantanis G. I., Young R. A., and Rowell R. M., “Swelling of wood, part II. Swelling in organic liquids”, ***Holzforschung***, 48: 480-490, (1994).

[13] Ermeydan M. A., Tomak E. D., “The Combined Effects of Boron and Polymer Modification on Decay Resistance and Properties of Wood”, ***16th International Materials Symposium***, Denizli, 1574-1581, (2016).

[14] Reinprecht L., Kizlink J., “Synthesis and anti-fungal screening test of organotin dithiocarbamates”, ***Drevársky Výskum***, 44: 67–74, (1999).

[15] Baldrian P.,"Interactions of heavy metals with white-rot fungi", ***Enzyme and Microbial Technology***, 32(1): 78-91, (2003).

[16] Gadd G. M., De Rome L., “Biosorption of copper by fungal melanins”, ***Applied Microbiology and Biotechnology***, 29(6): 610–617, (1988).

[17] Gadd G. M., Gray D. J., Newby P.J., “Role of melanin in fungal biosorption of tributyltin chloride”, ***Applied Microbiology and Biotechnology***, 34: 116–121, (1990).

[18] Palmans E., Mares G., Poppe J., Höfte M., “Biodegradation of xenobiotics by heavy metal resistant higher fungi”, ***Med Fac Landbouww Univ Gent***, 60: 2563, (1995).