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The study of selected properties of pine wood (*Pinus sylvestris* L.) subjected to acetylation

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Abstract: *The study of selected properties of pine wood (Pinus sylvestris* L.) *subjected to acetylation*. In the paper pine wood was subjected to acetylation with acetic anhydride and mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$. After modification process density, WPG index, water absorbability, volume swelling and colour of wood were carried out and compared with results obtained for unmodified pine wood. Based on the obtained results the density of acetylated pine wood was increased for each group of samples. The highest WPG index was obtained for previously dried wood modified with acetic anhydride (15.6%) or mixture of acetic anhydride and glacial acetic acid (10.5%). Acetylation process with acetic anhydride or mixture of acetic anhydride and glacial acetic acid of samples, which were extracted (in chloroform-ethanol $93:7_{w/w}$ mixture) and dried before modification, had beneficial effect on water absorbability of pine wood. These samples after 1001h (about 42 days) of soaking in water reached the lowest values of water absorbability (about 94%). Moreover, the volume swelling were significantly reduced for samples after double impregnation cycle (both in case of modification with acetic anhydride or mixture of acetic anhydride and glacial acetic acid). Wood after acetylation process was slightly darker than unmodified pine wood. Acetylation of samples, which were dried and soaked in DMF before modification, caused significant darkening of pine wood. The obtained colour was similar to colour of furfurylated wood (Kebony wood) or some of exotic species.

Keywords: glacial acetic acid, acetic anhydride, acetylation, wood properties, wood modification

INTRODUCTION

Wood is a biopolymer consists mainly of cellulose, hemicelluloses and lignin. Presence of these components results in high number of hydroxyl groups in this material which are responsible for unwanted wood properties when it is exposed to changes in humidity. These properties are: tendency to changing dimensions, initiation to cracking or lowering resistance to biological degradation. To reduce impact of this phenomena and enhance the properties of wood, various types of wood modification were developed.

Among many wood modification methods furfurylation, acetylation, in situ polymerization and thermo-hydro-mechanical densification can be distinguished [Rowell 2005, Hill 2006]. Acetylation is type of wood modification which is using acetic anhydride as a main substance. In suitable conditions acetic anhydride reacts with hydroxyl groups of wood cell wall components creating ester bond or causing bulking of cell wall which reduces access for water molecules, however by-product of this reaction is acetic acid which can cause acid hydrolysis of cellulose what results in strength loss of modified material [Rowell and Wallington 1983, Hill 2006]. In the past to modification process different catalysts like zinc chloride [Ridgway and Wallington. 1946], pyridine [Stamm and Tarkow 1947], N,N-dimethylformamide (DMF) [Clermont and Bender 1957] or even γ-rays [Svalbe and Ozolina 1970] were used. Nowadays acetylation process is carried out very often in liquid phase without using catalyst [Rowell 2005, Sun et al. 2019]. Moreover, acetic anhydride in acetylation process can be used also in gas phase, but then penetration inside wood is lower in comparison when liquid acetic anhydride is used [Rowell et al. 1986]. Furthermore, there is many factors which can influence acetylation process. The presence of water in wood can lead to reaction between acetic anhydride and water molecules [Rowell 2005]. Chemical

composition of used material has influence as well because cellulose, lignin and hemicelluloses reacts with acetic anhydride in different ways and presence of extractives can influence acetylation process leading to obtaining false results [Hill 2006]. Density of used material is important too since wood with low density has more porous structure which make it easier for acetic anhydride to go inside [Ajdinaj et al. 2013]

The wood after acetylation process has a lot of advantages. One of them is that acetylated wood is more hydrophobic. The acetylated wood has a lower amount of hydroxyl groups which results in better dimensional stability of this material. Moreover modification with acetic acid increases wood resistance to biological decay and sometimes can lead to obtaining higher hardness [Tarkow et al. 1955, Bongers and Beckers 2003, Rowell et al. 2009, Papadopoulos and Tountziarakis 2011]. Acetylation is the oldest wood chemical modification method used for commercial production by The Accoya™ plant at Arnhem in the Netherlands.

Softwood species as Scots pine (*Pinus sylvestris* L.) with their low (especially plantation species) or medium density and quite high porosity are great material for acetylation process since acetic anhydride can easily penetrate its structure and has better access to hydroxyl groups of wood components rather than hardwood species with higher density [Ajdinaj et al. 2013]. Moreover Scots pine is one of the mostly used and planted coniferous species in Europe what create easy accessible source of material.

This research was intended to study of selected properties of *Pinus sylvestris* L. wood subjected to acetylation with acetic anhydride. Additionally, in order to reduce costs, the addition of glacial acetic acid to acetic anhydride was checked in the acetylation process. After modification process the density (ρ), the weight percent gain index (WPG), the water absorbability (W), the volume swelling (K_v) and the colour of wood were determined.

MATERIALS AND METHODS

To the studies 162 pine wood samples (*Pinus sylvestris* L.) with dimensions of 20 x 20 x 30 mm and moisture content of 6.5% (drying-weight method) were prepared. The samples were divided into two series. The first one was dedicated for modification with acetic anhydride and the second one for modification with mixture of acetic anhydride and glacial acetic acid in the volume ratio of 50 to 50. 18 samples allocated for control group which was not modified.

The series of samples used to modification consisted of 10 groups of 18 samples each. Groups 1-4 were modified with acetic anhydride and groups 5-8 were modified with mixture of acetic anhydride and glacial acetic acid in the volume ratio of 50 to 50. Before acetylation process the groups were prepared in different ways. The wood samples from groups 1 and 5 were extracted in chloroform-ethanol mixture $(93:7)_{w/w}$ in Soxhlet apparatus for 20 hours in order to removing extractives. After that the samples were dried to constant mass at 103°C. For thus prepared samples mass and dimensions were measured. In turn, samples from groups 2 and 6 firstly were dried at 103°C to constant mass. Secondly, mass and dimensions of samples were measured and finally the samples were soaked in DMF for 1 hour. An excess of DMF from samples were eliminated using paper towels. The samples from groups 3 and 7 were only dried at 103°C to constant mass. After that a mass and dimensions of samples were measured. The samples from groups 4 and 8 were not dried and before modification process had moisture content of 6.5%. Also for these samples mass and dimensions were measured. Additionally, 2 groups of 18 samples (groups 9 and 10) were used to check the influence of double cycle of impregnation on wood properties. The samples from groups 9 and 10 were prepared in the same way as samples from groups 3 and 7.

Acetylation process consisted of impregnation, curing and extraction stages. During the impregnation stage samples were placed into bakers then flooded with acetic anhydride or

mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$, loaded with glass stoppers and placed in vacuum vessel. Then pressure was lowered for a period of 30 minutes and after that time it has been brought to normal conditions and samples were kept under this conditions for 90 minutes. In this way, the impregnation stage was performed for all samples. Whereas for samples from groups 9 and 10, after the first impregnation stage, an additional impregnation in the same conditions was carried out. In the curing stage, all impregnated samples were wrapped in an aluminum foil and then placed in a dryer. The curing stage was conducted at 130°C for 72 h. After that time an aluminum foil was removed and samples were dried at 103°C for 24 h. Finally, all samples were placed in Soxhlet apparatus and were extracted in acetone for 10 h in order to removing unreacted residuals of acetic anhydride or acetic acid. After that all samples were dried at 103°C for 24 h and for all samples mass and dimensions were measured.

After modification process the WPG index and density of control and modified samples were determined. The WPG index was estimated on mass of samples before (m_1) and after (m_2) modification process. The WPG index and density were determined based on measurements of 18 samples for each group. The WPG index was calculated using formula below:

$$WPG = \frac{m_2 - m_1}{m_1} \cdot 100\%$$

Whereas, the density of control and modified samples was calculated using the following formula:

$$\rho = \frac{m}{v}$$

where: m – mass of sample (kg),

v - volume of sample (m^3).

Water absorbability and volume swelling were calculated as well. Mass and volume of control and modified samples were measured after 5 min, 15 min, 60 min (1 h), 2400 min (40 h), 6000 min (100 h), 19740 min (329 h), 29880 min (498 h) and 60060 min (1001 h, about 42 days) of soaking in vessels filled with water. In order to prevent floating, samples were loaded with glass stopper. Before each measurement of samples mass and dimensions excess of water was eliminated using paper towels. The tests were carried out for 9 samples from each group.

Water absorbability was calculated using mass before soaking (m_1) and mass after soaking (m_2) according to the formula below:

$$W = \frac{m_2 - m_1}{m_1} \cdot 100\%$$

Volume swelling was calculated based on volume before soaking (v_1) and volume after soaking (v_2) using the following formula:

$$K_v = \frac{v_2 - v_1}{v_1} \cdot 100\%$$

Colour change test was carried out with ERICHSEN SPECTROMASTER 565-D spectrophotometer using CIEL* a* b* method [Mokrzycki and Tatol 2011]. This method is

using 3 coordinates (L*, a*, b*) and the difference between them is responsible for real colour of the specimen. Each coordinate defines different colour. Coordinate L* defines lightness (colour from white to black), coordinate a* defines colour from red to green and coordinate b* defines colour from blue to yellow. Colour changes were calculated with following formulas:

$$\Delta L^* = L^* - L_1^*$$

$$\Delta a^* = a^* - a_1^*$$

$$\Delta b^* = b^* - b_1^*$$

where coordinates without index (L*, a*, b*) were average values obtained for modified samples and coordinates with index 1 (L^*_1, a^*_1, b^*_1) were average values obtained for control samples. All analyzed colour parameters (L*, a*, b*) were measured 4 times for each sample.

The total colour change (ΔE) was calculated with following formula:

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2}$$

RESULTS AND DISCUSSION

In the paper *Pinus sylvestris* L. wood was subjected to acetylation process. In Table 1 the results of density and weight percent gain index obtained for *Pinus sylvestris* L. wood before and after acetylation process with using acetic anhydride or mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$ were presented.

Table 1. Results of density and weight percent gain index obtained for *Pinus sylvestris* L. wood before and after acetylation process.

Group	Group label	ρ (before modification) [kg/m^3]	ρ (after modification) [kg/m^3]	WPG [%]
ACETIC ANHYDRIDE				
1	EXTRACTED and DRIED	562 ± 48	586 ± 46	13.1 ± 2.9
2	DRIED and DMF TREATED	563 ± 41	585 ± 31	10.7 ± 1.6
3	DRIED	557 ± 51	582 ± 47	15.6 ± 1.6
4	HUMID	552 ± 35	577 ± 37	8.2 ± 1.3
9	DRIED (2x IMPREGNATED)	531 ± 40	551 ± 35	15.1 ± 2.4
ACETIC ANHYDRIDE + GLACIAL ACETIC ACID				
5	EXTRACTED and DRIED	567 ± 33	580 ± 31	7.2 ± 1.3
6	DRIED and DMF TREATED	576 ± 27	587 ± 25	3.8 ± 0.7
7	DRIED	562 ± 45	575 ± 46	10.5 ± 0.5
8	HUMID	528 ± 46	544 ± 46	5.3 ± 0.9
10	DRIED (2x IMPREGNATED)	537 ± 48	542 ± 47	10.3 ± 1.0
0	Control	527 ± 50	-	-

Based on the results presented in Table 1 it can be observed that the density of *Pinus sylvestris* L. wood before modification was in range from 527 kg/m^3 to 576 kg/m^3. Acetylation process caused a slightly increase of density values which were in range from 542 kg/m^3 to 587 kg/m^3. In majority of cases a higher values of density were obtained for samples modified with acetic anhydride than for wood samples modified with mixture of acetic anhydride and glacial acetic acid.

Another studied parameter for chemically modified wood was WPG index. For samples modified with acetic anhydride values of WPG index were in range from 8.2% to 15.6% and were higher than for samples modified with mixture of acetic anhydride and glacial acetic acid (3.8% to 10.5%). The lower values of WPG for samples modified with mixture of acetic anhydride and glacial acetic acid can come from too high concentration of acetic acid (about 50%) used in the experiment, which probably slowed down the modification process. According to literature it is known that an acetic acid concentrations in the impregnation solution up to 10-20% can accelerate the acetylation reaction due to the swelling effect of the acetic acid [Rowell 2005, Ajdinaj et al. 2013]. The higher concentrations of acetic acid have the opposite effect. Moreover there was no significant differences in WPG index values obtained for samples with double impregnation cycle. In comparison, Rowell [2005] for southern pine modified with acetic anhydride at 140°C during 180 min obtained higher WPG index which was 22.1%. Also, Sun et al. [2019] for *Pinus sylvestris* var. *mongolica* Litv. wood modified with acetic anhydride at 120°C (time of acetylation from 0.5 h to 8 h) obtained higher results of WPG index (13.6% - 22.3%).

In this paper the highest values of WPG index were obtained for previously dried samples modified with acetic anhydride (15.6%) or mixture of acetic anhydride and glacial acetic acid (10.5%). On the other hand, among the results obtained, significantly lower values of the WPG index were noticed for samples pretreated with DMF and next modified with acetic anhydride (10.7%) or mixture of acetic anhydride and glacial acetic acid (3.8%). Also, a low WPG index results were obtained for non-dried samples (6.5% humidity), both acetylated with acetic anhydride (8.2%) or with a mixture of acetic anhydride and glacial acetic acid (5.3%). In this case a low values of WPG index were caused probably by side reactions of DMF or water with acetic anhydride or acetic acid. Hence, the acetylation process was much less efficient.

In Figs 1-2 the results of water absorbability and volume swelling for unmodified and modified pine wood were presented. Based on the obtained results it can be observed that in mostly cases water absorbability and volume swelling were lower for acetylated samples (excluding group 6) in comparison to unmodified pine wood. The water absorbability and volume swelling of control samples after 60060 min (1001h, about 42 days) of soaking in water were 114.7% and 16.9% respectively. Among the samples modified with acetic anhydride, the group 9 obtained the lowest value of volume swelling which was 5.5%. This is the advantageous result of double impregnation cycle. For samples modified with acetic anhydride, where only single cycle of impregnation was implemented, group 1 (extracted and dried wood before acetylation) after 60060 min (1001h) of soaking in water reached the lowest water absorbability and volume swelling which were 93.9% and 9.7% respectively. Slightly higher values were obtained for group 3 (dried wood before modification), which after 60060 min (1001h) of soaking in water reached the water absorbability and volume swelling on the level 96.7% and 9.8% respectively.

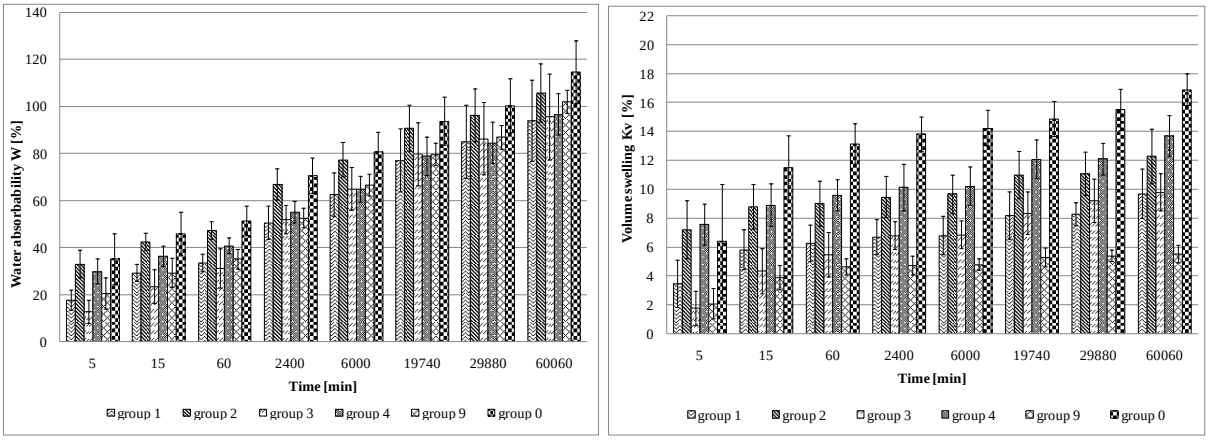

Fig. 1. Water absorbability and volume swelling of unmodified *Pinus sylvestris* L. wood and modified with acetic anhydride in different systems

In case of samples modified with mixture of acetic anhydride and acetic acid similar co-relations were observed. For samples from group 10, where double cycle of impregnation was implemented, after 60060 min of soaking in water the lowest value of volume swelling was obtained (7.2%). The lowest value (94.0%) of water absorbability after 60060 min of soaking had samples from group 5 (extracted and dried wood before acetylation). For samples from group 6 (dried and soaked wood in DMF before modification) values of water absorbability and volume swelling were 113.3% and 18.7% respectively. These values were one of the highest among all the studied groups. Moreover, the value of volume swelling (for samples from group 6) was higher than this obtained for unmodified pine wood.

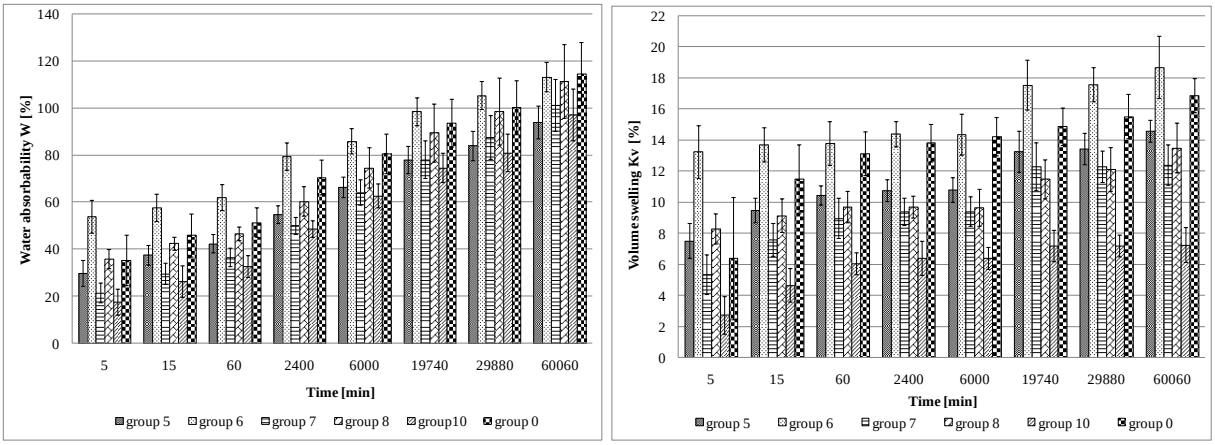

Fig. 2. Water absorbability and volume swelling of unmodified *Pinus sylvestris* L. wood and modified with mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$ in different systems

In Fig. 3 the colour changes of *Pinus sylvestris* L. wood after acetylation process were presented. Based on the obtained results it can be noticed that pine wood after acetylation became darker ($\Delta L < 0$). Analogical effects were obtained by Dong et al. [2016], who also studied acetylation process. As a result of acetylation of pine and poplar wood at 120°C (time of acetylation was 4 h), the color of the wood became slightly darker.

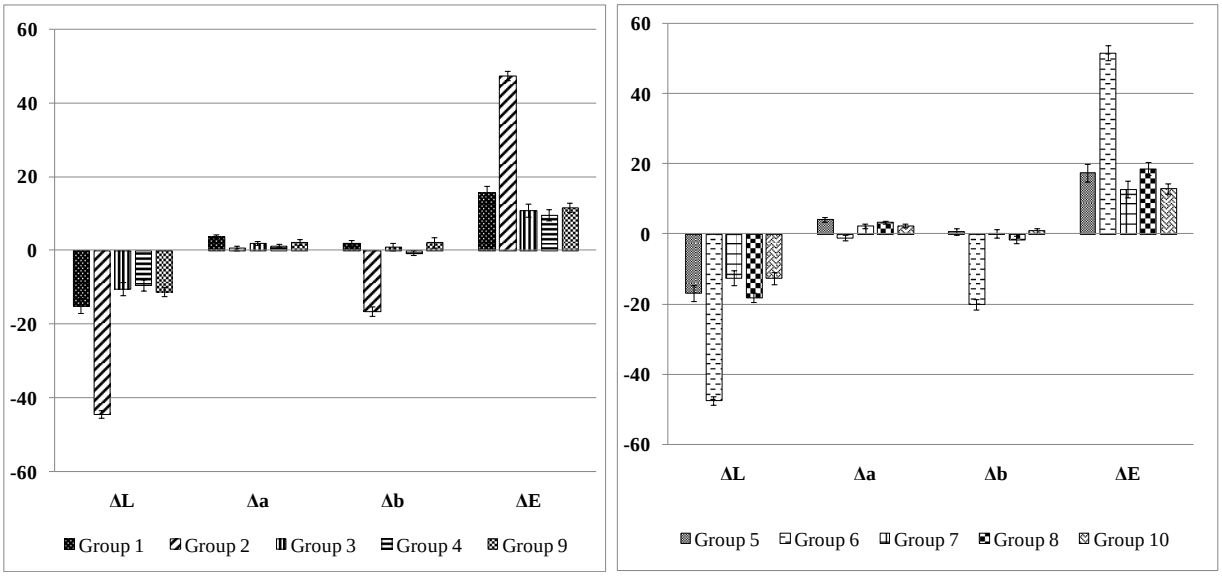

Fig. 3. Colour changes of *Pinus sylvestris* L. wood after acetylation.

In this paper the most colour changes were observed for samples from groups 2 and 6 (dried and soaked wood in DMF before modification). After acetylation process it was obtained material, which had dark brown colour similar to furfurylated wood (Kebony wood) or some of exotic species. The colour of samples from the rest of groups was generally similar to each other and differences between them were hard to observe with the naked eye. Moreover, no significant influence of double impregnation was observed on the colour of the tested wood (compare the samples from groups 3 and 9 or 7 and 10). However, based on the colorimetric analysis (Fig. 3), it turned out that the acetylated pine wood with the mixture of acetic anhydride and glacial acetic acid was slightly more darker than wood modified with the acetic anhydride alone.

To sum up, this research showed that acetylation process can improve selected properties of pine wood. In majority of studied groups the increased density of wood and decreased water absorbability or volume swelling were observed in comparison to unmodified pine wood. Moreover it was noticed that implementation of double impregnation cycle has beneficial effect for obtained results of volume swelling. Nevertheless many factors have influence acetylation process so it should be done carefully.

SUMMARY AND CONCLUSIONS

- Acetylation caused increase of pine wood density.
- Based on the obtained data, modification with acetic anhydride had more beneficial effect on pine wood properties rather than modification with mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$. It can be result of usage too high concentration of glacial acetic acid in this modifying solution.
- The highest results of WPG index were obtained for previously dried samples modified with acetic anhydride or mixture of acetic anhydride and glacial acetic acid. Double impregnation cycle did not influence this parameter.
- Implementation of double impregnation cycle (both in case of acetic anhydride or mixture of acetic anhydride and glacial acetic acid) significantly decreased volume swelling in comparison to unmodified pine wood.
- Acetylation with acetic anhydride or mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$ of samples, which were extracted and dried before modification had beneficial effect on water absorbability of pine wood. After 60060 min (1001h, about

42 days) of soaking in water the samples reached the lowest values of water absorbability.

- Acetylation with acetic anhydride or mixture of acetic anhydride and glacial acetic acid $(50:50)_{v/v}$ of samples, which were dried and soaked in DMF before modification caused significant darkening of pine wood. In the rest of cases the modified wood was slightly darker than unmodified pine wood.

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Streszczenie: *Badanie wybranych właściwości drewna sosnowego (Pinus sylvestris* L.) *poddanego acetylowaniu*. W tej pracy drewno sosnowe poddano acetylowaniu przy użyciu bezwodnika octowego oraz mieszaniny bezwodnika octowego i lodowatego kwasu octowego w stosunku objętościowym 50:50. Po procesie modyfikacji zbadano gęstość, współczynnik WPG, nasiąkliwość, spęcznienie objętościowe i barwę drewna, a następnie porównano z

wynikami uzyskanymi dla niemodyfikowanego drewna sosnowego. Na podstawie uzyskanych wyników stwierdzono, że dla każdej z grup gęstość acetylowanego drewna sosnowego była wyższa niż gęstość drewna przed modyfikacją. Najwyższy współczynnik WPG uzyskano dla wstępnie suszonego drewna modyfikowanego bezwodnikiem octowym (15,6%) lub mieszaniną bezwodnika octowego i lodowatego kwasu octowego (10,5%). Proces acetylowania przy użyciu bezwodnika octowego lub mieszaniny bezwodnika octowego i lodowatego kwasu octowego próbek, które przed procesem modyfikacji zostały wyekstrahowane (w mieszaninie chloroform-etanol 93:7$_{m/m}$) i wysuszone, miał korzystny wpływ na nasiąkliwość drewna sosny. Próbki te po 1001 godzinach (około 42 dniach) moczenia w wodzie osiągnęły najniższe wartości nasiąkliwości (około 94%). Ponadto, spęcznienie objętościowe zostało znacznie obniżone dla próbek poddanych podwójnemu cyklowi impregnacji (zarówno w przypadku próbek zmodyfikowanych przy użyciu bezwodnika octowego lub mieszaniny bezwodnika octowego i lodowatego kwasu octowego). Drewno po acetylowaniu było nieco ciemniejsze od niemodyfikowanego drewna sosny. Acetylowanie próbek, które przed modyfikacją zostały wysuszone i moczone w DMF, spowodowało znaczne pociemnienie drewna sosny. Uzyskany kolor był podobny do koloru drewna furfurylowanego (drewno Kebony) lub drewna niektórych gatunków egzotycznych.

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