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Modification of some Albanian wood properties through chemical treatment

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A study was carried out to evaluate the influence of acetylation on physical properties and gluing ability of some Albanian woods. Three woods were studied: beech (*Fagus sylvatica L.*), poplar (*Populus alba L.*) and fir (*Abies alba Mill.*). For acetylation, pyridine and acetic anhydride were used. After treatment, all the samples were conditioned to 100% relative humidity of air and were measured according to radial and tangential directions. After that, the samples were ovendried and were weighed and measured again, calculating the shrinkage and wood percent gain. Again, the samples were reconditioned to 100% relative humidity of air, calculating the swelling. The volumetric shrinkages of acetylated poplar and beech resulted 4.05 and 8.5%, meanwhile for non acetylated samples 9.8 and 16.5%. Tangential shrinkage of acetylated fir was 2.2% and for non acetylated 6.5%. The volumetric swellings of acetylated poplar and beech resulted 4.2 and 9.3%, meanwhile for the non acetylated 10.8 and 19.8%. Tangential swelling of acetylated fir wood was 1.7 and 5.8% for non acetylated. It seems that acetylation reduced more than 50% the moisture-related dimensional changes of wood. Regarding gluing the shear strength of acetylated beech resulted 2.4 times less comparing with non acetylated one.

Key words: Acetylation, gluing, shrinkage, strength, swelling, wood.

INTRODUCTION

Wood is a hygroscopic material, sensible to atmospheric humidity changes and it can be submitted to considerable dimensional changes according to its grain directions. Its swelling and shrinkage values are different according to the sectional cut. Swelling and shrinkage values in tangential direction are almost twice bigger than those of radial direction, while in axial direction these values are inconsiderable (Giordano, 1981). These dimensional changes can cause splits or deformations.

Improvement of dimensional stability of wood has always been a primary interest, because its swelling and shrinkage's tendency, caused by variations of humidity, is considered its most negative property. Dimensional changes of wood caused by moisture content changes are considerable. Wood's cell wall swells about 45% from the 0% moisture content to saturation fibres point (Skaar, 1988). In tangential directions, the shrinkage from green to 6% moisture content varies from 4 to 9%, while in radial direction, for the same conditions, varies from 1.8 to 6% (Kollmann and Côté, 1968). This can cause deformations and splits to wood boards, during their drying and their use. With the aim to improve its dimensional stability and to reduce its volumetric changes, the wood has been modified by means of different methods.

One of the main methods that reduce the dimensional

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changes of wood is acetylating (Rowell, 2006). This method consists in chemical treatment and has been industrially applied since 1961 in boards used in buildings (Rowell, 1985*).* According to this technique, one hydroxyl group (–OH) of wood is substituted by a radical CH_3COO of an anhydride acetic molecule $(CH_3CO)_2O$. This substitution reduces the number of free positions –OH that can react with water molecules, reducing the water sensibility of wood. The reaction of wood's acetylation can be presented below:

Wood-OH + CH_3-CO-O-CO-CH_3 → Wood-O-CO-CH_3 + CH_3-COOH

Chemically, hydroxyl group (–OH) can be found to the functional groups of phenol, benzene and carbohydrate alcohols. The alcoholic hydroxyls can be primary or secondary, while the phenols can be connected with aromatic chains which contain different types of substitutes. As result, each of these groups can present a different reaction regarding anhydrite.

The reaction's product between anhydrite acetic and wood is acetic acid (HOac). It is known that a concentration of acetic acid lower than 10%, accelerates the reaction and the opposite happens for higher concentration (Navi and Heger, 2005). The size of radical CH_3-CO-O is bigger than of hydroxyl group (–OH), causing so the swelling of wood at the beginning of the treatment. According to results regarding to pine wood, is noted that acetyl treatment increases more than 55% the dimensional stability of wood, but reduces about 50% its tensile modulus (Ramsden et al., 1997). It is found that anti shrinkage efficiency (ASE) of acetyl treated pine, spruce, birch and beech arrive from 45 to 50%, and the module of elasticity and rupture are reduced about 15% (Epmeier et al., 2001; Epmeir et al., 2003). Other studies show that Brinell hardness of acetylated pine is increased up to 20%, but Janka hardness is not significantly affected (Larsson and Simonson, 1994; Papadopoulos and Tountziarakis, 2011).

This treatment improves wood's resistance against biodegradation and colour changes (Imamura, 1993; Sakuragawa, 1996; Nasheri et al., 2005; Papadopoulos et al., 2010; Mohebby and Militz, 2010). Tests have proven a good resistance against termite attacks and marine organisms (Suttie et al., 1999; Westin et al., 2004). Besides this, wood's darkening does not happen, which characterise resins treatments.

Regarding to the method mentioned above, a study is carried out to evaluate the influence of acetylating on physical properties (specifically shrinkage and swelling) and gluing ability of some of the most important Albanian woods. It aims to give information about opportunities of application of this treatment, especially for outdoor applications, as well as for a better selection of wood material, referring to Albanian native woods. It is motivated by increasing demand for high quality and long-term performance wood products. The study is focused respectively:

(i) For physical properties; on beech wood (*Fagus sylvatica* L.), poplar (*Populus alba* L.) and fir (*Abies alba* Mill.). These species are selected taking into account that they are the most important species used in Albania. The research is focused on both groups of softwoods and hardwoods. Also, a comparison is made between species from the same group, but noticeably with different density (poplar with beech).
(ii) For gluing; on beech wood (*F. sylvatica* L.). This selection is conditioned because beech is the main wood used for production of solid wood based panels not only in Albania, but in many other countries of the region, and also, gluing is one of the most important chains of their production.

MATERIALS AND METHODS

The study was based on comparative laboratory method, cause-consequence (Creswell, 2003). The method consisted of quantity evaluation of a specific phenomenon caused by a provocative factor and after that, the evaluation of the same phenomenon in the situation of the factor's absence. In our case, the phenomenon was the dimensional variability (shrinkage and swelling), and the provocative factor was the acetylation of the sample. Laboratory tests consisted in preparation of samples, treatment (acetylation), conditioning of samples in different conditions of relative air humidity and measurements of their dimensional changes as well as tests of gluing shear strength. The study was carried out at the Faculty of Forestry Sciences of Tirana, during the period February-June 2009.

Preparation of samples

Regarding to physical properties, the samples were selected from pieces of kiln dried boards without deformations or structure defects. For each wood, there was selected one single board's piece. From each piece, one strip with dimensions of section 2 × 1 cm, and length the same as the piece of board, was sawn. After that, the strips were sawn in pieces with dimensions 2 × 1 × 1 cm and then the pieces were cut in samples by a single use microtome knife. The samples presented clear radial, tangential and cross-sections, with dimensions in longitudinal and tangential directions 1 cm, whereas their dimension in radial direction varied from 0.5 to 1 cm (Figure 1). All samples were marked with numbers, taking into account their positions in pieces. Samples with odd numbers were acetylated, respectively 48 for beech, 44 for fir and 38 for poplar. With regard to gluing, the samples were prepared from beech boards without deformations or structure defects, which could have influence on gluing resistance. Pieces with dimensions 5 × 2 × 1 cm, and with grain direction parallel with the longer edge were produced. The pieces were weighed and selected in couples, in manner that pieces with approximate density could be glued together. Their faces had to present flat and smooth surfaces. Thickness tolerance higher than 0.1 mm was not permitted, making possible a good pressure during the hardening of glue. Based on the standard EN 205 (Determination of tensile shear strength of lap-joints), the pieces were selected with angles from 30° to 90° between annual rings and bonding surface (EN205, 1991). Almost half of them were acetylated.

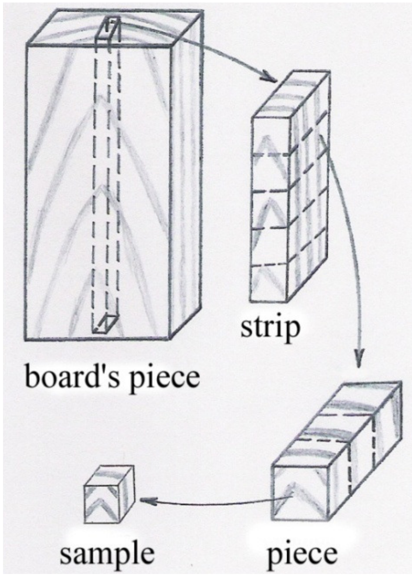

Figure 1. Preparation of samples.

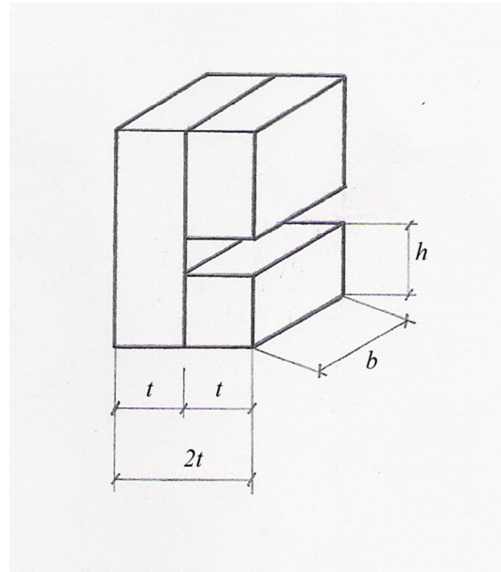

Figure 3. Finished samples. *h* – height of test's surface, *b* – width of test's surface, *2t* – width of test piece.

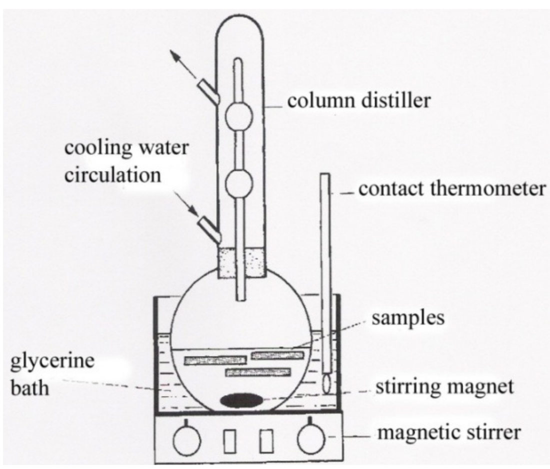

Figure 2. The acetylating system.

Acetylation and tests

Acetylation was performed according to the laboratory procedure, adequate for small dimension samples with a total weight of 150 g (Navi and Heger, 2005). Oven dried samples were weighed and after that they were soaked in a mixture of acetic anhydride and pyridine. There was 500 ml acetic anhydride used (95%, MERCK, Germany) for acetylation and 900 ml pyridine (99%, MERCK, Germany) as catalyst. The wood-liquid system was kept in 90°C for 4 h. The boiling point of pyridine was between 114 and 116°C, requiring the utilisation of a system for cooling and steams circulation. The system used for acetylation is showed in Figure 2. After 4 h, the samples were taken off from the balloon and were cooled down. After that, the measurement points on tangential and radial faces were marked on all acetylated or not acetylated small samples, selected for physical properties study, and after were conditioned. Conditioning consisted in three steps:

(i) 100% relative humidity of the air: Dessicator was used. To create an environment with 100% humidity of the air, the bottom of the dessicator was filled with distilled water and after was applied the vacuum –0.9 atm. The samples stayed in these conditions until they reached equilibrium state, which corresponds to the fibers saturation point, and by means of an indicator they were measured according to tangential and radial directions. It must be noted that fir's samples were not measured in radial direction, because their dimensions were higher than the measurement's step of indicator.
(ii) Oven drying in temperature 103 ± 1°C, until they reached equilibrium state, corresponding to 0% moisture content. After that, the samples were weighed and measured again. Weight percent gain (WPG) and shrinkage was calculated.
(iii) 100% relative humidity of the air and after respective measurements, the swelling was calculated. Volumetric swelling (αv) was calculated below:

$$\alpha_V = \frac{\beta_V}{1 - \frac{\beta_V}{100}}$$

β_V – volumetric shrinkage for each sample.

With regard to gluing tests, the procedure continued thus:

(1) After treated pieces were cooled down and the smell was removed, they were oven dried, weighed and equilibrated to environment room conditions. WPG of acetylated pieces resulted 13.5%,
(2) Application of adhesive. PVA glue (NEON, Albania) was used. The quantity of glue was referred to industrial application, from 170 to 240 g/m^2, resulting in 0, 2 g per piece. It was verified by weighing the pieces before and after application of glue,
(3) Pressure. It was applied with hand grip vice for 24 h,
(4) Preparation of samples and tests.

There were prepared 32 acetylated samples (test pieces) and 37 non-acetylated. After gluing, canals were sawed on samples, as shown in Figure 3. The samples were tested with a mechanical test

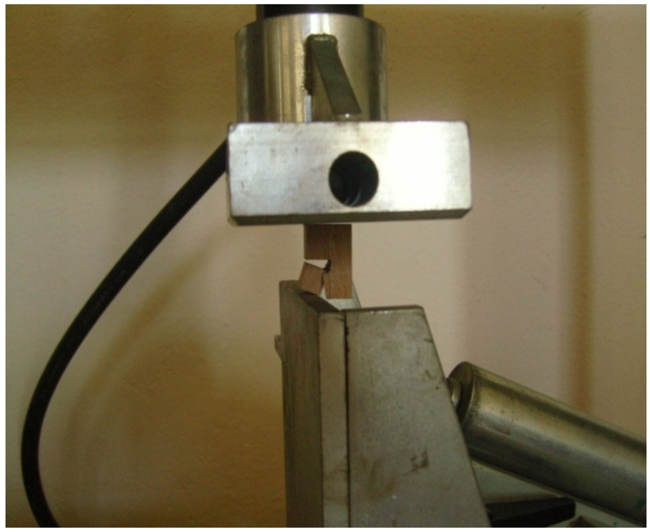

Figure 4. Testing photo.

Table 1. Results of shrinkage.

Wood species	Treatment	Weight gain (%)	Stand. dev.	Radial shrink.	Stand. dev.	Tang. shrink.	Stand. dev.	Volum. shrink.	Stand. dev.
Fir	Untreated	0	-	-	-	6.5	2.99	-	-
	Acetylated	21	1.07	-	-	2.2	0.59	-	-
Poplar	Untreated	0	-	3.3	0.45	6.4	0.41	9.8	0.64
	Acetylated	20.6	0.4	1.3	0.25	2.7	0.4	4.05	0.48
Beech	Untreated	0	-	4.9	0.54	11.6	0.64	16.5	1.02
	Acetylated	13.6	0.92	2.6	0.16	5.9	0.64	8.5	0.65

machine (CONTROLAB, France) to rupture (Figure 4). The shear resistance of gluing for each test was calculated:

$$S = F/A \text{ [N/mm}^2\text{]}$$

F- rupture load [N], A- gluing surface [mm^2].

RESULTS

Table 1 summarised results of shrinkage for three studied species present, while Table 2 shows results of swelling. Table 3 summarised results of gluing tests present.

DISCUSSION

The volumetric shrinkages of acetylated poplar and beech resulted 4.05 and 8.5%, meanwhile for non acetylated samples the shrinkages were 9.8 and 16.5%. According to these results, anti shrinkage efficiency (ASE) resulted, respectively 59% for poplar and 49% for beech. The tangential shrinkage of acetylated fir was 2.2% and for non acetylated 6.5%. About volumetric swellings, acetylated poplar and beech resulted 4.2 and 9.3%, meanwhile the non acetylated resulted 10.8 and 19.8%. Anti swelling efficiency resulted respectively 61% for poplar and 53% for beech. Tangential swelling of acetylated fir wood was 1.7 and 5.8% for non acetylated.

It was noted that acetylation reduced moisture-related dimensional changes of poplar and beech wood more than 50%. The treatment's efficiency for poplar was almost 10% higher than beech. Taking into consideration results of other studies, we can say that the efficiency of acetylation depends on wood density. Much greater to be the density, smaller is the effect of acetylation (Rowell et al., 1986; Beckers and Militz, 1994). This means that in woods with high density, the acetyl molecules penetrate with more difficulty, making possible the blockage of a smaller number of free hydroxyl (–OH) groups comparing to low density woods. Also, it must be noted

Table 2. Results of swelling.

Wood species	Treatment	Weight gain (%)	Stand. dev.	Radial swell.	Stand. dev.	Tang. swell.	Stand. dev.	Volum. swell.	Stand. dev.
Fir	Untreated	0	-	-	-	5.8	0.85	-	-
	Acetylated	21	0.77	-	-	1.7	0.37	-	-
Poplar	Untreated	0	-	3.2	0.44	6.1	0.52	10.8	0.79
	Acetylated	20.6	0.4	1.5	0.21	2.5	0.43	4.2	0.52
Beech	Untreated	0	-	5.2	0.24	12.5	0.89	19.8	1.45
	Acetylated	13.6	0.92	2.5	0.13	5.8	0.73	9.3	0.78

Table 3. Results of gluing tests.

Treatment	Weight gain (%)	Standard deviation	Mean value of shear strength (N/mm^2)	Standard deviation
Untreated	0	-	6.72	0.95
Acetylated	13.5	0.73	2.79	0.67

that concentration of impregnation solution is another factor which play a significant role on the treatment degree (Keskin et al., 2013).

Regarding gluing tests, the shear strength of acetylated wood was reduced by 59%. The destruction of samples happened to the adhesive layer, typically for weak gluing. In case of a good adhesion, wood near the adhesive layer will be destroyed, but not the adhesive layer. A good adhesion gives a higher resistance than glued wood. From results we can say that adhesion of acetylated wood with PVA glues can be classified as not qualitative. A recent study shows that acetylated finger jointed beech wood produced with PVA glue, present lower values of bending strength comparing with those of non acetylated (Papadopoulos, 2008). However, cross-linking PVA glues develop bonds of high shear strength of acetylated wood, in tests of dry strength (Rowell, 2005).

In general, the results of the study are compatible with those findings in literature regarding to the effect of acetylation on different wood species. As expected wood's acetylating is a chemical modification with clear positive effects on dimensional stability (Rowell, 2006). It improves notably the physical properties of wood reducing the tendency of interchanges with air humidity. From all other modifications developed to improve the dimensional stability of the wood, this method offers the highest advantages, because of small negative impact on others desirable properties of wood (Epmeir et al., 2003, Korkut, 2008).

It seems that Albanian woods react very well regarding to this modification, opening so a positive perspective for industrial application for windows, stairs and outside doors. The efficiency of acetylation related to dimensional changes is more than 50%. Considering the demand of timber as raw material for constructions in Albania, the acetylated wood appears as a product which presents many advantages. By the other side, acetylation reduces some of wood's technological properties like ability of gluing. Application of PVA glues with acetylated beech is not advisable, because in this case the reduction of gluing resistance is more than 50%, excluding this combination for industrial structural applications.

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