RIGA TECHNICAL UNIVERSITY
Faculty of Materials Science and Applied Chemistry
Institute of Polymer Materials

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IMPROVEMENT OF THE PROPERTIES OF BIRCH PLYWOOD WITH THERMO-HYDRO TREATMENT METHOD

Summary of the Doctoral Thesis

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**THE DOCTORAL THESIS
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To be granted the scientific degree of Doctor of Engineering Sciences, the present Doctoral Thesis has been submitted for the defence at the open meeting on 21 September 21 2016 at 3 p.m., at Riga Technical University, Faculty of Materials Science and Applied Chemistry, 3 P. Valdena Street, Room 272.

The Doctoral Thesis is available at the Scientific Library of Riga Technical University, 5 P. Valdena Street, Riga, LV-1048 and the National Library of Latvia, 3 Mukusalas Street, Riga, LV-1423.

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DECLARATION OF ACADEMIC INTEGRITY

I hereby declare that the Doctoral Thesis submitted for the review to Riga Technical University for the promotion to the scientific degree of Doctor of Engineering Sciences is my own and does not contain any unacknowledged material from any source. I confirm that this Thesis has not been submitted to any other university for the promotion to other scientific degree.

Juris Grīniņš ………………

Date: ………… 2016.

The Doctoral Thesis has been written in Latvian; it contains Introduction, Literature Review, Experimental Part, Results and Discussion, Conclusions and Bibliography with 231 reference sources. The Doctoral Thesis has been illustrated by 40 figures, 39 tables and 32 equations. The total volume of the Thesis is 155 pages, including 6 appendices.

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CONTENTS

ABBREVIATIONS AND NOTATIONS

ASE – anti-swelling efficiency
BS – bending strength
CA – contact angle
CWTWC – cell wall total water capacity
CWU – capillary water uptake
C_{CWU} – coefficient of capillary water uptake
DP – degree of polymerization
EMC – equilibrium moisture content
experimental plywood – plywood made from thermo-hydro treated birch veneers using phenol-formaldehyde laminate as adhesive
HB – Brinell hardness
ML – mass loss
PF – phenol-formaldehyde adhesive
reference plywood – thermo-hydro treated industrial birch plywood
RM – relative moisture
ST – swelling in thickness
THT – thermo-hydro treatment (thermo-hydro treated – depending on the context of the sentence)
TM – thermal modification (thermally modified – depending on the context of the sentence)
TS – tensile strength
VS – volumetric swelling
WRE – water resorption efficiency

GENERAL DESCRIPTION OF THE PRESENT RESEARCH

The existence of a sustainable society requires renewable materials, reduced use of natural non-renewable materials and considerable restriction of environment affecting factors. One variant how to decrease the carbon dioxide emissions is to enhance the volume of wood products use and their service properties, so that the carbon is stored in the material for a longer period of time. Another variant is to substitute energy-intensive materials with wood and its products. Substituting non-renewable materials with wood based ones, it is necessary to know how to develop and introduce new treatment processes for wood products, with a low impact on the environment. To make wood competitive with other materials, it should be not only environmentally friendly, but also competitive in terms of technical and service properties and easy-to-utilize, with economically grounded use. The development of thermal modification (TM) processes and their application for wood products could be the deciding factor for the further development of the wood protection avenue.

Forests are among the main natural resources of Latvia and occupy 3260 thousand ha, which is 92 % of the total forest area. From this, 34 % is covered with pine, 31 % with birch, 18 % with spruce, 10 % with alder, 5 % with aspen, and ~1 % with oak and ash. The forest area and the wood resources stored there are not diminished, but continue to grow [1]. Within 2009–2013, the total wood stock in forests had reached 667 million cubic meters. The annual growth of wood resources in Latvia exceeds 25 million cubic meters. The forest field in Latvia is one of the most important fields of the national economy, and its proportion in the gross domestic product makes up ~6 %. The forest field, in terms of production and export (20 % of the state total export), is one of the largest manufacturing sectors in Latvia’s national economy, and the proportion of its added value in the manufacturing industry made up 23.1 % in 2013. According to the 2015 data, the export of plywood constitutes 8.8 % of Latvia’s total forest production export, and it is exported to countries such as Germany, the Netherlands, France and Turkey [2].

Birch (*Betula spp.*) plywood is widely used in building, internal and external finishing, construction of transport vehicles, containers, sports gear, furniture, packaging material, toys, and bed strips production, but its application in outdoor and high humidity conditions is limited because of the poor biological durability (the lowest – durability class 5 according to EN 350-1) [3]. The effect of wood degrading fungi and humidity are the factors that essentially impair the technical properties of plywood – bonding and mechanical strength, and board surface quality. In service, plywood durability is determined by several factors: veneer wood, adhesive, pressing regimes, environmental conditions (humidity, temperature fluctuations, etc). Moisture easily penetrates into veneer layers, they swell and waves are formed on the plywood surface. The water uptake is decreased, covering the plywood with hydrophobic (water repelling) laminate; however, this does not prevent from degradation by fungi. To improve the biodurability, the veneers or plywood are impregnated with biocide-containing compositions; those can also be introduced into the adhesive, but the compatibility of the amount of biocide, required for wood protection, with the adhesive is complicated. Impregnating the plywood plates, the most essential problems are the uneven distribution of biocides (only the veneer external layers soak well), and the fact that quality soaking is only for thin (6.5 mm) materials, which are not used in load bearing structures. Sawing impregnated industrial size plates to the sizes intended for end use, the internal less protected veneer edges are exposed to the effect of fungi. Impregnation efficiency is difficult to predict, because heartwood soaks worse than sapwood, but their ratio in veneer sheets is different. The plywood from hardwood veneers is even more difficult to be protected against biodegradation in the outdoor environment than coniferous wood-based materials. TM, in comparison with the chemical modification or protection with biocides, is an ecological method for the improvement of the physical and biodurability properties of wood without the environment and people hazardous TM compounds.

In Europe and worldwide, the coniferous wood TM process has been much investigated; there is less information about hardwood, but progress during the past 5 years is observed also in this direction. Little information is available on the veneer or plywood TM, especially with sample sizes, which are appropriate to small pilot plants (0.5–1 m^3). As the optimal treatment temperature for deciduous (birch, beech, aspen, poplar, and other species) wood, the range of 180 °C to 220 °C is common. At such temperatures, it was possible to reach a significant growth in biodurability and dimensional stability, but mechanical strength considerably decreased. It can be concluded from the practical experience that, for a thin material such as veneer, the same treatment conditions (temperature and time) as for solid wood cannot be applied automatically. In the modification environment, under the effect of temperature, pressure and environment acidity, the veneers become very brittle. Therefore, in the present research low treatment temperatures and short treatment times for birch veneer thermo-hydro treatment (THT) were used.

To evaluate the THT plywood service properties, untreated wood product (lumber, parquet, cladding, slabs, etc.) testing standards were used for characterizing water uptake, mechanical strength, biological durability and surface properties.

Topicality of the Research

Plywood and TM wood producers intend to extend the offered range of new high value-added products that will be able to fill specific market niches. However, no TM plywood product is found in the offer of the European and Latvian TM wood producers. This testifies that this market niche is still free and has a future potential.

There is little information on the plywood and veneer TM in the literature. Therefore, the investigation of this method is a logical step in the search for new products with improved properties. Plywood, intended for use in constant or regularly high humidity conditions, will enable the manufacturer to occupy a new market niche in accordance with the service properties and effectively compete with the analogous biocide-containing products, taking into account various significant environmental aspects, of which the most important are: work with chemical preservatives in plywood production, potential environment pollution during the service and possible utilization problems after the product's life cycle end. TM in a steam environment at elevated pressure is a promising technique for the improvement of plywood properties to create a product for use in a humid environment and outdoor conditions.

Aim of the Doctoral Thesis

Development of a new wood product – plywood with significantly better functional properties, ensuring reduced moisture and water uptake, improved dimensional stability and durability against degradation by rot fungi, without biocides and surface laminating, in order to extend the applicability at construction sites and in the transport industry under high humidity and outdoor conditions.

To reach the aim, the following tasks are set:

- to choose THT regimes appropriate for veneers based on the literature data and practical experience with the goal of obtaining plywood with improved properties under high humidity and outdoor conditions;
- to perform the birch veneer and industrial plywood THT in a laboratory experimental pilot plant in a water steam environment at two treatment temperatures (150 °C and 160 °C) and two holding times (10 min and 50 min) at these temperatures;
- to determine THT veneer properties;
- to determine the THT industrial birch plywood properties;
- to glue THT veneers under conditions approximated to industrial ones;
- to determine the properties of the plywood obtained from THT birch veneers;
- to compare the properties of the obtained THT plywood products with each other and with those of the untreated plywood;
- to determine the optimum method and process parameters for obtaining THT plywood based on the gained data.

Thesis Statements to Be Defended

- By the THT method, it is possible to obtain a new plywood product using two different technological methods – industrial plywood THT and veneer THT, using further gluing with the adhesive.
- The obtained THT plywood product conforms to the use class 3 (EN 335) [4] and durability class 2–3 against rot fungi (CEN/TS 15083-1) [5]; it has an improved dimensional stability, a lower equilibrium moisture content, with small mechanical strength losses.

Scientific Novelty

- THT of birch veneers and industrial birch plywood at a low treatment temperature and a short holding time, compared with the information available in the literature, has been performed.

- The veneer THT has been carried out in conditions, much more approximated to those of the industrial process (number of sheets, size and packing principle), compared with the hitherto performed studies, and it has been glued in semi-industrial conditions with a commercially available adhesive.
- Different THT veneer properties before the gluing with the adhesive have been determined.
- For the first time in history of the TM processes at the same heat treatment parameters, 2 different technologies have been used to obtain THT plywood, and a comprehensive study and a mutual comparison of the properties of the obtained products have been carried out.

Practical Significance of the Research

1. The results of the research can be used for developing the THT birch plywood technology to establish production, which would enable obtaining new plywood products with a high added value.
2. Optimum THT regimes for veneers have been developed, which allow obtaining plywood according to the use class 3 (EN 335-1), for use in outdoor conditions without contact with soil, with the durability class 2 to 4 against rot fungi (CEN/TS 15083-1), with improved dimensional stability, reduced wood equilibrium moisture content, surface hydrophility and water uptake through it, and promising mechanical properties.

Approbation of the Research Results

The author has presented the scientific achievements and results related to the theme of the Doctoral Thesis at 8 international scientific conferences. On the theme of the Doctoral Thesis, there are 12 publications in conference proceedings and books of abstracts, and 9 articles in peer-reviewed journals (1–9): *Holzforschung, International Wood Products Journal, International Biodeterioration & Biodegradation, Journal of Analytical and Applied Pyrolysis*.

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SUMMARY OF THE DOCTORAL THESIS

In the Introduction, the topicality of the Doctoral thesis is stated, the goal and tasks are formulated, and the guidelines of the Doctoral Thesis are set out.

The first chapter is devoted to the literature review, indicating the types of wood protection, and a survey of the development of the wood thermal modification (TM) process is performed. The origin of veneer modification is considered, and the most appropriate modification types are determined. The theoretically most suitable types of modification for plywood and some existing studies on the plywood TM are described. The main wood TM techniques used worldwide and their technological characteristics are compared, and the production volumes and tendencies in Europe and worldwide are indicated. The advantages and drawbacks of TM wood, and the changes in the physico-mechanical properties, biological durability and other properties as a result of TM in connection with the changes in the wood chemical composition are summarized.

The second chapter is devoted to the experimental part, in which the choice and preparation of veneer and plywood samples as well as the production of plywood from THT veneers are justified, and the methods and equipment used in the research are reflected. The principal scheme used for obtaining THT veneers and plywood in the Doctoral Thesis is shown in Fig. 1. The description of the used multifunctional wood modification equipment is given. Two different THT temperatures and two different holding times at each temperature are selected (Table 1).

Table 1

Selected Regimes for THT of Birch Veneers and Plywood

Treatment regime	Max temperature (°C)	Treatment time at T_{max} (min)	Max pressure in process (MPa)	Heating/ cooling speed (°C/min)
1	150	10	0.472	0.12–0.22 / 0.20–0.40
2	150	50	0.495	
3	160	10	0.637	
4	160	50	0.660	

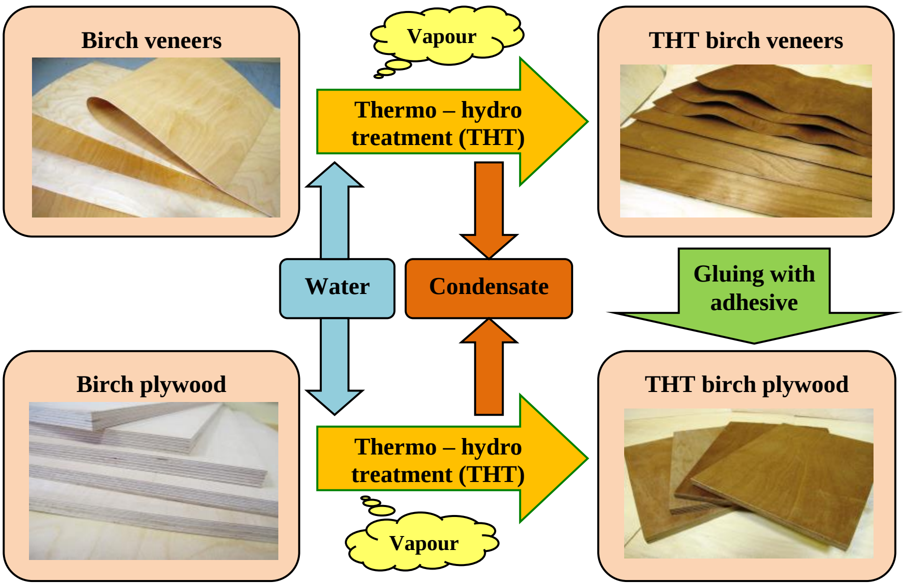

Fig. 1. Principal scheme for acquisition of THT birch plywood.

The veneer and plywood THT process, depending on the process parameters, can be divided into three stages: I – heating; II – holding at the temperature; III – cooling (Fig. 2).

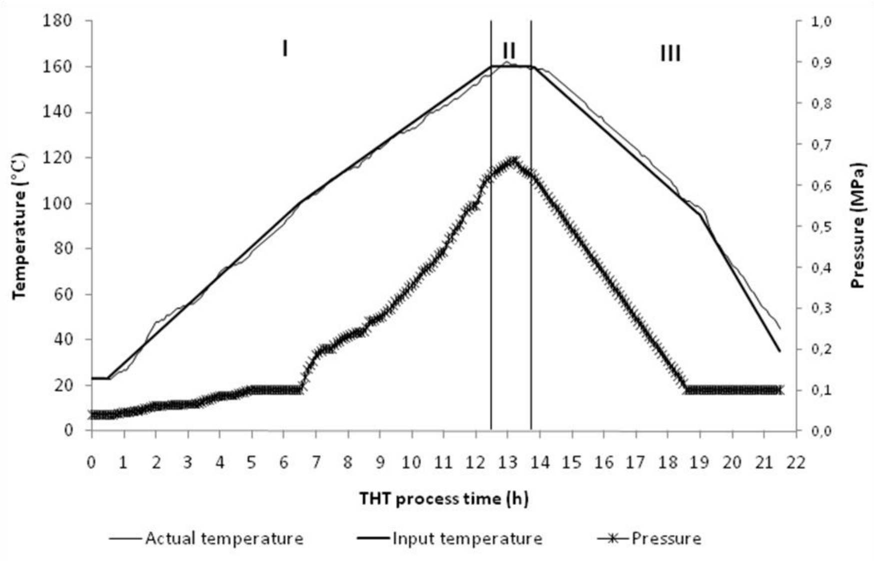

Fig. 2. Diagram of THT process at the treatment regime of 160°C / 50 min.

In the Doctoral Thesis, the analytical methods for characterizing THT veneers are used:

- chemical composition and elements composition;
- equilibrium moisture content;
- mechanical strength (static bending and tensile strength);
- biodurability against rot and stain fungi;
- surface contact angle and color.

In the Doctoral Thesis, analytical methods for characterizing THT industrial plywood (reference) and plywood made from THT veneers (experimental) are used:

- physical parameter changes;
- equilibrium moisture content;
- anti-swelling efficiency;
- water uptake through the surface;
- swelling in thickness and bending strength after the cyclic testing;
- mechanical strength (static bending strength and Brinell hardness);
- bonding strength;
- biodurability against rot and colour fungi;
- surface contact angle and surface quality.

In the third chapter, based on the information summarized in Chapters 1 and 2, the results of the research are analysed and their evaluation is given.

In Conclusions, the achieved results of the research are stated and the main findings are defined.

In Bibliography, the literature sources used in the Doctoral Thesis are listed, on the basis of which the research directions have been identified and the obtained results compared.

RESULTS AND DISCUSSION

THT Veneers

As a result of THT, the chemical composition of veneer changes (Table 2), mass losses (ML) are formed, which increase with increasing treatment temperature and time. It is known that the ML during the wood TM is caused by the evaporation of water, extractives and hemicelluloses destruction products [6]. Temperature has a greater effect on the formation of extractable substances, and increase by 10 °C increases the extractives content in veneer more than twice.

Table 2

Mass Loss and Chemical Composition of THT Birch Veneers

Measured data	Control	Treatment temperature (°C) / time (min)			
		150/10	150/50	160/10	160/50
Mass loss (%)	-	1.6 ± 1.0	2.4 ± 1.0	4.3 ± 0.9	6.3 ± 1.0
Extractives (%)	2.3 ± 0.4	3.2 ± 0.5	5.2 ± 0.3	10.2 ± 0.9	12.5 ± 1.1
Lignin (%)	21.3 ± 0.2	21.8 ± 0.2	23.1 ± 0.8	23.0 ± 0.9	24.4 ± 0.6
Kürschner cellulose (%)	50.8 ± 0.8	57.7 ± 0.1	57.9 ± 0.5	61.4 ± 0.3	65.4 ± 1.0
Holocellulose (%)	67.3 ± 0.6	63.7 ± 0.5	64.2 ± 1.3	67.6 ± 1.5	71.1 ± 0.2
α-cellulose	43.9 ± 0.7	46.7 ± 0.5	48.7 ± 1.5	53.0 ± 1.7	56.7 ± 0.6
Hemicelluloses* (%)	23.4 ± 0.7	17.0 ± 0.5	15.5 ± 1.5	14.6 ± 1.7	14.4 ± 0.6
Methoxy group content (%)	5.50 ± 0.01	5.76 ± 0.04	5.89 ± 0.10	5.93 ± 0.08	6.11 ± 0.06
Cellulose DP	930 ± 10	880 ± 10	940 ± 30	1180 ± 50	1160 ± 30

*Hemicelluloses = Holocellulose - α-cellulose

The relative lignin content in the THT veneer also grows as a function of the treatment temperature and time. Relative Kürschner cellulose content in THT veneer increases significantly – at the 150 °C treatment by ~7 %, but at 160 °C by 11–15 %. The holocellulose content in veneer at the 150°C treatment decreases by 3–4 %, but at the maximum treatment (160/50) increases up to 71.1 % (~4 % increase). The untreated veneer contains 43.9 % of α-cellulose, and the THT at 150 °C causes an increase by 2.8 % (150/10) and 4.8 % (150/50). At 160 °C, the increase is even more pronounced – 9.1 % (160/10) and 12.8 % (160/50). The untreated veneer contains 23.4 % of hemicelluloses. After the treatment at 150 °C, the hemicellulose losses are 27 % after 10 min and 34 % after 50 min. At 160 °C, the losses are 38 % (160/10) and 39 % (160/50).

The amount of methoxy groups in THT veneer wood slightly increases. This testifies that there has been no significant cleavage of methoxy groups as a result of TM, and the increase is related to the increase in the relative lignin content in THT wood.

The THT at 160 °C considerably increases the DP of cellulose, which is favored either by the transfer of the amorphous regions of the cellulose structure (with lower DP) into crystalline ones or also a significant destruction of the amorphous part of cellulose.

As a result of THT, veneer becomes significantly more hydrophobic, its equilibrium moisture content (EMC) decreases at all the environmental RM contents (Fig. 3). The EMC content in THT veneer is more than 1.5 times lower than that in the control. All THT regimes, even at the highest RM, provide the veneer EMC content much below 20 %.

THT causes a substantial decrease in the veneer bending (BS) and tensile strength (TS) (Fig. 4). BS decreases up to 19 %, but the TS is 2–3 fold lower than the control. Cellulose and lignin seem to have a greater impact on ensuring BS, but hemicelluloses are more responsible for TS. As indicated by the veneer chemical composition (see Table 2) hemicelluloses are thermally more affected than other wood components and, therefore, the TS is expected to be more affected in the THT process than the BS.

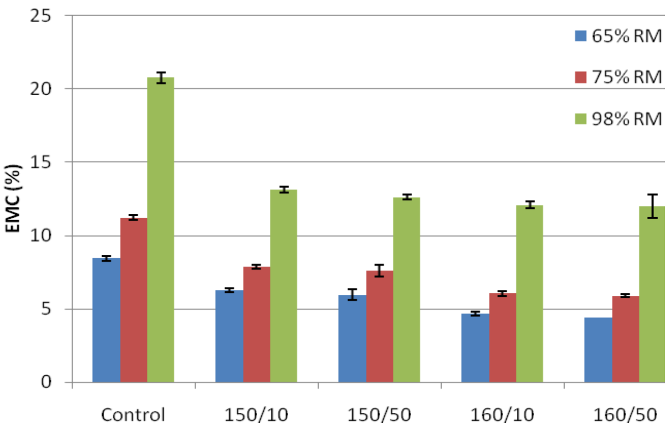

Fig. 3. EMC of THT veneer at different RM contents.

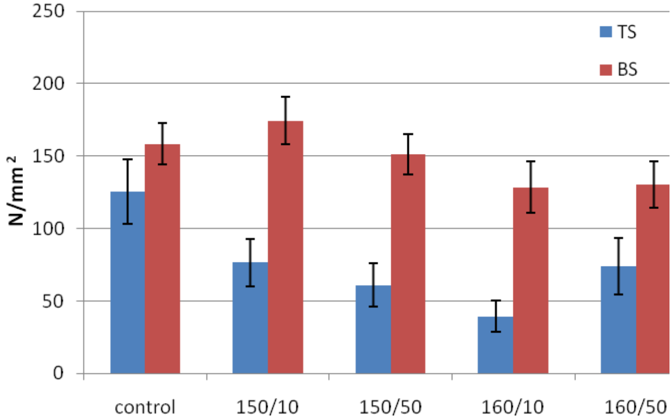

Fig. 4. Bending strength (BS) and tensile strength (TS) of THT birch veneer.

The results of rot fungi tests of THT veneer are summarized in Table 3. For the veneer, the ML (both ENV 12038 and combined EN 84+ENV 12038 test) is higher after exposure to *C. puteana*. In the ENV 12038 test, the worst biodurability against *C. puteana* is for the THT veneer 150/10 (43 %), but in the case of *T. versicolor*, ML is ~29 % for the control and the treatments 150/10, 150/50. Also the 160 °C treatment is not effective.

In the combined EN 84 + ENV 12038 test, the THT veneer at 150/50 has the worst biological durability against *C. puteana* (40.7 %), but for both treatments 150/10 and 150/50, the worst durability is against *T. versicolor* (18 %). The smallest ML is for the THT veneer at 160/50. THT veneer is not very durable against the effect of rot fungi, because the ML is greater than 5 %.

Table 3

Decay Resistance – ML of THT Birch Veneer after Attack by the Brown Rot Fungus *Coniophora Puteana* and the White Rot Fungus *Trametes Versicolor*

Treatment temperature (°C) / time (min)	ENV 12038		EN 84 un ENV 12038 (after leaching)	
	C. puteana	*T. versicolor*	*C. puteana*	*T. versicolor*
Control	36.6 ± 3.5	29.6 ± 3.4	30.6 ± 5.6	9.7 ± 3.4
150/10	43.0 ± 6.8	29.3 ± 4.2	31.3 ± 8.6	18.4 ± 6.0
150/50	38.6 ± 4.9	28.8 ± 8.0	40.7 ± 6.6	18.8 ± 4.9
160/10	29.1 ± 4.4	19.6 ± 5.0	27.9 ± 2.2	12.1 ± 3.7
160/50	30.7 ± 12.5	18.1 ± 5.5	18.7± 6.6	6.7 ± 3.0

The evaluation of the THT veneer surface overgrowing with mould and blue stain fungi is given in Table 4. The control samples had more than 50 % surface overgrowing; the THT veneer depending on the treatment regime was not colonized at all or was slightly overgrown with white air mycelium. After the mycelium residue removal, the fungi-induced staining was not observed for THT veneer (rating 0), while the control samples were strongly stained (rating 4). Thus, the fungi development on the samples was hindered by THT.

Table 4

Growth of Mould and Blue Stain Fungi on THT Birch Veneer

Measured data	Control	Treatment temperature (°C) / time (min)			
		150/10	150/50	160/10	160/50
Rating (0–4)	4	0	0	0	0

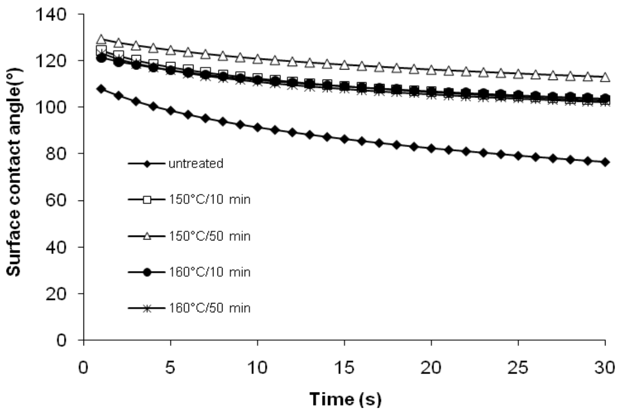

Fig. 5. Surface contact angles of THT birch veneer.

THT veneer has a reduced surface wetting with water (Fig. 5). The contact angle (CA) values after the 150 °C treatment increase by 19.1–26.6 %, but after the 160 °C treatment by 17.6 %. Also over time, after the drop filling, for all THT veneer samples, CA is greater than that for the untreated veneer, and it remains above 100° even after 30 seconds, but it is less than 80° for the control, testifying rather hydrophilic properties.

THT Plywood and Plywood Produced from THT Veneer

After THT, the ML occurs in birch plywood (reference) (Table 5). At 150 °C, the ML is negligible, but at 160 °C, the ML is 2–4 fold higher. After the THT, the plywood density decreases, but the volume remains practically unchanged and the PF adhesive is assumed to ensure the shape stability during the treatment.

Table 5

Changes in the Physical Parameters of Birch Plywood after THT

Treatment temperature (°C) / time (min)	Density (kg × m^{-3})		Density loss (%)	Mass loss (%)	Volume changes (%)
	Before	After			
150/10	730 ± 6	708 ± 17	4.0 ± 0.6	2.0 ± 0.7	−1.1 ± 0.7
150/50		700 ± 18	4.7 ± 0.5	2.0 ± 1.2	−0.1 ± 0.7
160/10		676 ± 22	6.9 ± 0.9	4.5 ± 1.1	1.5 ± 0.7
160/50		659 ± 15	9.0 ± 0.8	7.4 ± 0.9	1.5 ± 0.4

THT veneers were glued with PF laminate in semi-industrial conditions. For the obtained material (experimental plywood), density after the gluing is determined (Table 6).

Table 6

Density (ρ) of Experimental Plywood Produced from THT Veneer

Measured data	Control	Treatment temperature (°C) / time (min)			
		150/10	150/50	160/10	160/50
ρ (kg × m^{-3})	680 ± 16	740 ± 20	708 ± 14	806 ± 33	871 ± 36
$\Delta\rho$ (%)	-	+8.8	+4.1	+18.5	+28.1

All experimental plywood samples glued from THT veneer have a higher density than those obtained from the untreated veneer. Since all samples were subjected to the same pressing-gluing regime: temperature of 140 °C; pressing time of 15 min; pressure of 1.2 MPa, the gluing technology in all cases can be considered to be identical. It should be concluded that the densification of THT veneer occurred in the gluing-pressing process. It has a favorable effect on the bending strength of the experimental plywood (see Fig. 13), but slightly limits the anti-swelling efficiency (see Fig. 8).

EMC is a very important wood characteristic, because it influences other properties such as mechanical strength, dimensional stability and biodurability. The EMC for reference and experimental plywood is reduced at all environmental RM (Fig. 6). For experimental plywood, EMC is lower in all cases. The THT temperature has a greater effect than the processing time. For the experimental plywood, EMC decreases by 19–38 %, 17–35 % and 4–12 % at 65 %, 75 %, and 98 % RM, respectively. For the experimental plywood, the decrease at 150 °C is 38–48 %, but at 160 °C, EMC is twice lower than in the case of the untreated material.

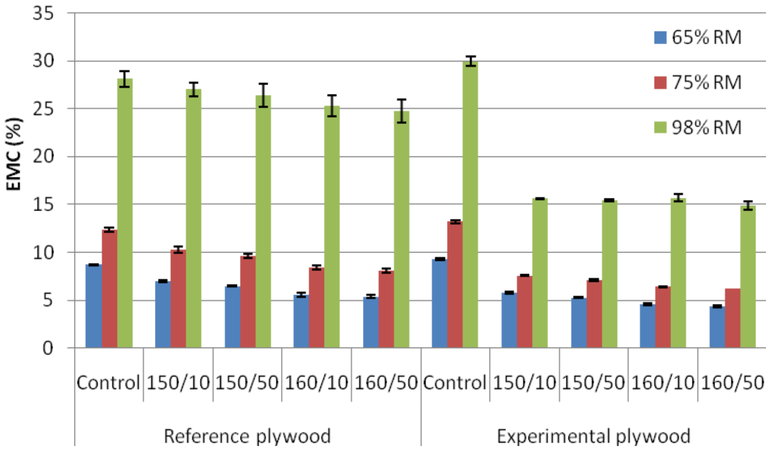

Fig. 6. EMC of reference and experimental plywood at different RM contents.

In most cases decreased EMC in the wood after THT improves dimensional stability. After THT dimensional stability is improved for both plywood types. For the reference plywood, ASE increases with the increase of both the THT temperature and time (Fig. 7). At 160 °C, THT samples have similar dimensional stability throughout the whole test, and their ASE considerably exceeds that of the 150 °C samples. After the 1st cycle, the ASE at 160 °C for THT samples is by 13–26 % higher than that at 150°C and by 15.8–28.1 % higher after the 5th cycle. However, after each cycle, the ASE decreases for all the samples, and after the 5th cycle, the decrease of ASE for THT samples is 39–50 % at 150 °C, but 26–27% at 160 °C.

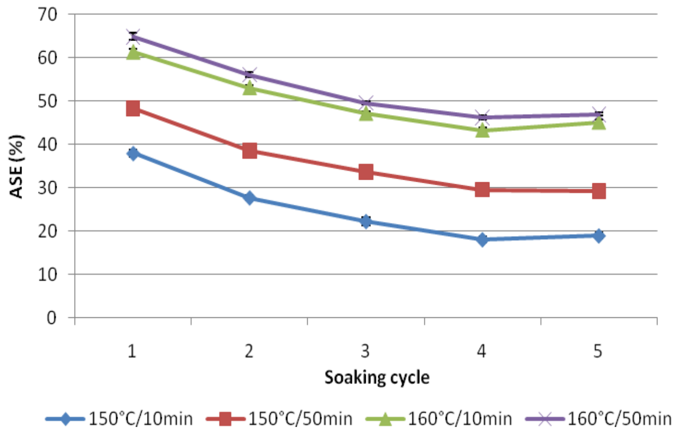

Fig. 7. ASE of reference plywood during 5 soaking – drying cycles.

The experimental plywood has no tendency indicating the effect of temperature or time on the material ASE (Fig. 8). The smallest ASE is at 150 °C/10 min, but the greatest at 150 °C/50 min for THT samples. At the 160 °C treatment, the best properties are for the 160/10 samples, with the ASE after the 5th cycle close to that of the best sample (150/50). The 160/50 treatment results in a slightly worse ASE. In the case of the best sample (150/50), the ASE after each cycle decreases, and after the 5th cycle, the losses reach 10.1 %. For the worst sample (150/10), ASE is significantly improved, and after the 5th cycle, the improvement is 47.4 %. For the 160/10 sample, ASE after 5 cycles slightly increases (+1.7 %), but in the case of 160/50, decreases by 16.2 %.

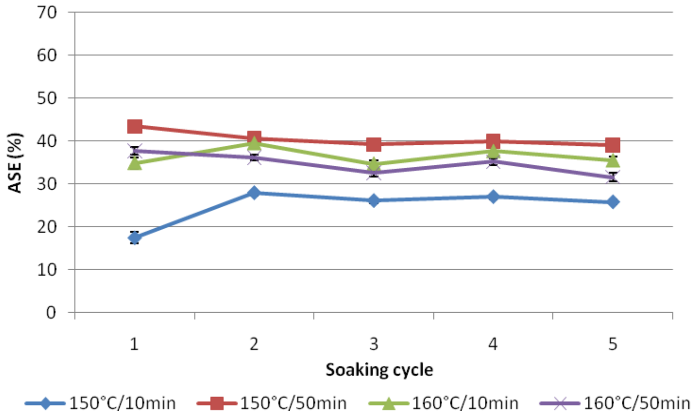

Fig. 8. ASE of experimental plywood during 5 soaking – drying cycles.

As a result of THT, the equilibrium moisture content of the plywood decreases, the material hydrophobicity increases and dimensional stability improves. The plywood water uptake through the surface is assumed to drop.

For the reference and experimental plywood, the water uptake through the surface decreases with increasing both the THT temperature and treatment time (Figs. 9 and 10). For experimental plywood, the water uptake through the surface is much lower and does not reach 1000 g/m^2 at the end of the test, but it exceeds 2000 g/m^2 (150/10) for the reference plywood.

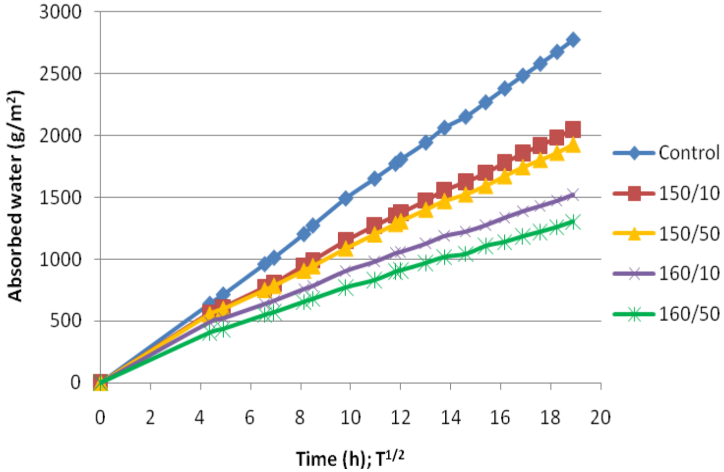

Fig. 9. CWU of reference plywood through the surface.

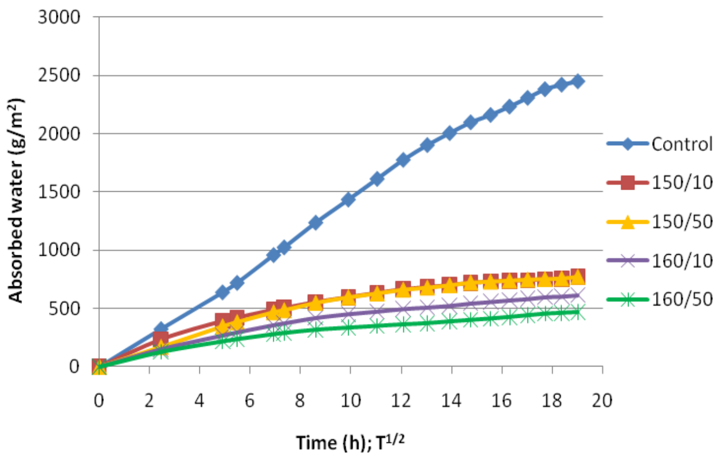

Fig. 10. CWU of experimental plywood through the surface.

In order to determine the changes in the plywood water uptake through the surface after weathering in the outdoor blue stain – mould test, also the water uptake through the weathered surface was tested. For all reference and experimental samples, water uptake during the same test period is greater than before weathering (Figs. 11 and 12). For the experimental plywood the water uptake through the surface after the weathering is considerably lower than for the reference plywood.

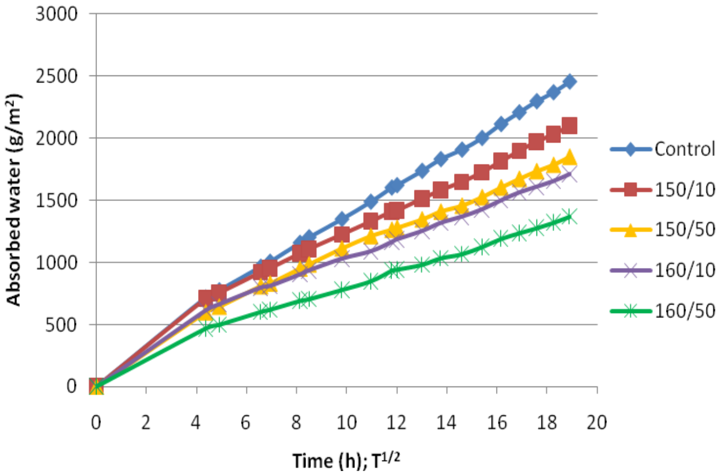

Fig. 11. CWU of reference plywood surface after exposure to mould and blue stain fungi growth in outdoor conditions.

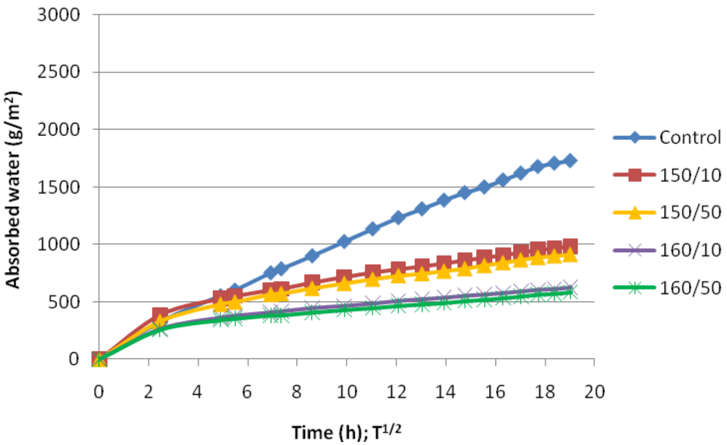

Fig. 12. CWU of experimental plywood surface after exposure to mould and blue stain fungi growth in outdoor conditions.

Bending strength (BS) is an important index, and it is known that it significantly declines as a result of the wood TM [7]. BS is a combination of the three stresses – tensile, compressive and shear. The BS of the reference and experimental plywood is shown in Fig. 13. Even the lowest THT temperature at 150 °C causes the decrease of BS by 15–21 %; after the 160 °C treatment, the BS losses reach 46 % after 50 min treatment. THT time is just as a significant contributory factor as temperature.

For the experimental plywood, BS even improves compared to that of the untreated material. BS for the regime 150 °C / 10 min improves by 25 %, but the improvement for both treatments at 160 °C is 28–33 %. Only for the regime 150 °C/50 min, the improvement is relatively negligible – 8 %. The BS improvement is explained by the material density, which is greater for all the experimental samples glued from THT veneers than that of the samples obtained from untreated veneers (see Table 6).

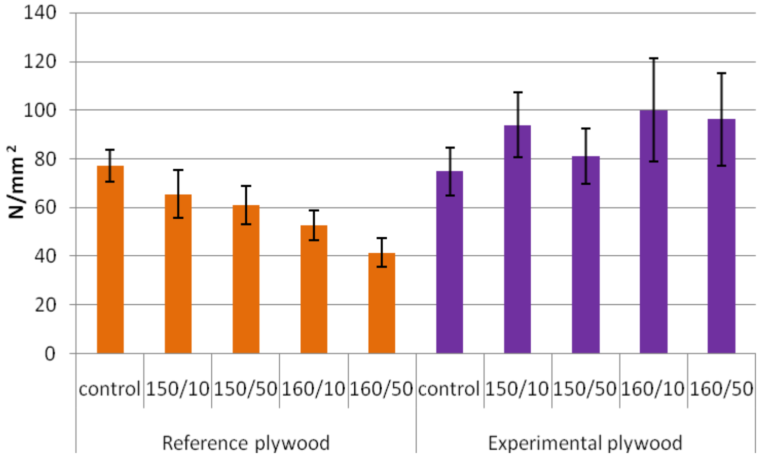

Fig. 13. Bending strength of reference and experimental plywood.

Brinell hardness (HB) for the reference plywood considerably decreases, but the difference between all the treatment regimes is statistically insignificant (Fig. 14). It cannot be determined, which of the treatment parameter has a greater effect on HB, and its decrease is 33–45 %.

For experimental plywood HB decreases but to a lesser extent than for the reference plywood. At the 150 °C treatment, the decrease of HB is 13–23 %, but for the 160 C treatment – 6–10 %. HB does not correlate directly with the material density, because the highest HB is for the untreated sample with the lowest density.

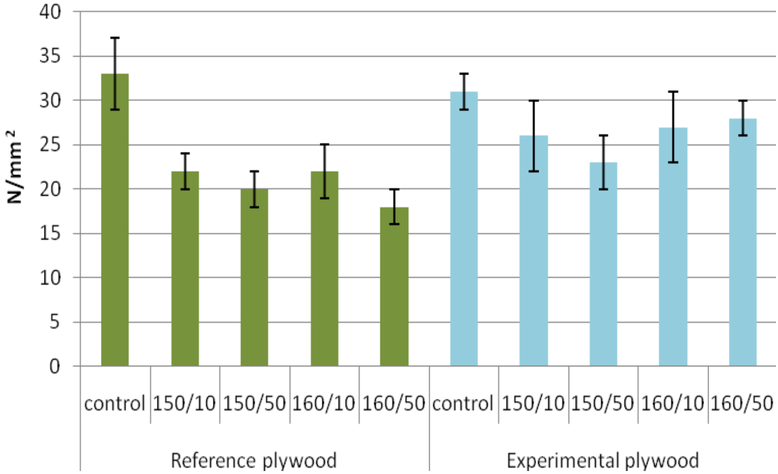

Fig. 14. Brinell hardness of reference and experimental plywood.

For both THT plywood products, bonding strength (shear strength) is assessed in accordance with the Standard EN 314 [8] requirements, carrying out cold water (24H) and boiling water pre-treatment (4H + 20H + 4H). According to the Standard EN 636 [9] requirements, the bonding strength must be higher than 1 N × mm^{-1} for the materials designed for use in outdoor conditions (use class 3).

For the reference plywood, the bonding strength is considerably lower than that for the experimental one (Fig. 15), and the average values do not reach 1 N × mm^{-1}. For the ordinary birch plywood, glued with the PF glue, bonding strength is 2.53 and 2.07 N × mm^{-2} after the cold and boiling water pre-treatment. THT at 150 °C causes the bonding quality degradation of more than half (54–64 %), while for the treatments at 160 °C, the decrease exceeds 70 %. Subjecting the industrial plywood to THT, the glue layers are degraded and such modification is not acceptable in production.

The bonding strength of all experimental plywood samples corresponds to class 3 (plywood usable in outdoor conditions). Bonding strength is more affected by the treatment temperature than time. Increasing the THT temperature from 150 to 160 °C, the bonding strength after the 24H pre-treatment declines by 27 % if the treatment duration is 10 min, and by 14 % if the treatment duration is 50 min. The changes after the 4H + 20H + 4H pre-treatment are 31 % (10 min) and 28 % (50 min), respectively. The greatest bonding strength is demonstrated by the plywood samples glued from the 150/10 THT veneer.

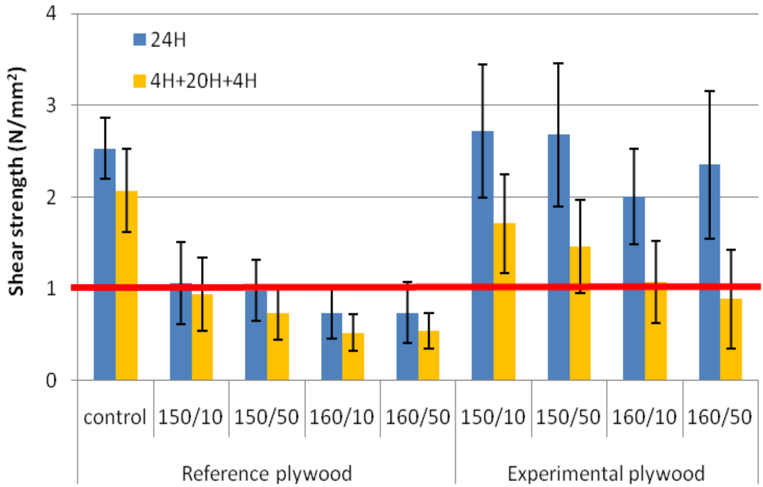

Fig. 15. Bonding quality of reference and experimental plywood.

For TM wood products, a very important indicator is their biodurability against the rot fungi. In the case of ENV 12038, the best durability against rot fungi is for untreated plywood, and it is classified as very durable (Fig. 16). THT does not improve the biodurability, and ML increases, which is explained by the formation of degradation products (for example, easily utilizable sugars) suitable for the development of fungi in the treatment process. Although the ML for the THT samples is greater than that for the control, they are also classified as very durable, except for the 150/50 treatment.

After the leaching with water (EN 84 + ENV 12038), the greatest ML is for untreated plywood after attack of both rot fungi (non-durable or slightly durable). The durability against rot fungi grows with raising the THT temperature and time. The best results were achieved after the THT at 160 °C / 50 min, and the material was moderately durable against *C. puteana* and durable against *T. versicolor*. THT at 150 °C gives only a minor improvement, and the material is slightly durable.

After long-term evaporation in wind tunnel (EN 73 + ENV 12038), the greatest ML is for the untreated plywood, and it is classified as very durable. From the THT samples, only the 150/10 sample is durable after the *T. versicolor* exposure, but others are very durable. The best results are achieved by the treatment at 160 °C, for which ML is lower than without weathering. This suggests that part of the fungi-growth-enhancing compounds is evaporated from the samples.

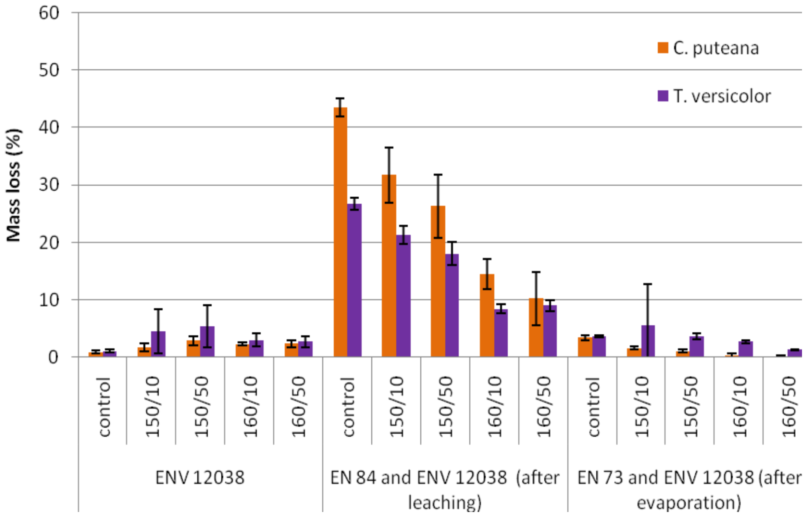

Fig. 16. Decay resistance – ML of reference plywood after attack by the brown rot fungus *Coniophora puteana* and the white rot fungus *Trametes versicolor.*

For experimental plywood at the same THT regimes, almost in all cases, ML is greater than that for the reference plywood (Fig. 17). In the ENV 12 038 case, the best durability against rot fungi is for the untreated plywood, which is very durable. THT does not improve the biodurability but significantly impairs it. After the 150 °C treatment, the material is non-durable or slightly durable. Also both 160 °C treatments give only a slightly durable or medium durable material. The presence of degradation products suitable for the development of rot fungi in the plywood glued from THT veneer facilitates their development in comparison with the case of the reference plywood.

After leaching with water (EN 84 + ENV 12038), there is a similar tendency as for the reference plywood. The greatest ML is for the untreated plywood after the effect of both rot fungi, and it is non-durable. The durability against rot fungi slightly increases with elevating the THT temperature and time. The best results were achieved treating veneers in the 160 °C / 50 min regime, and it was possible to obtain slightly durable plywood against *C. puteana* and durable against *T. versicolor*. The THT at 150 °C gives only a slightly durable material.

After long-term evaporation in wind tunnel (EN 73 + ENV 12038), the lowest ML is for the untreated plywood, and it is very durable. All THT samples have a significantly lower biodurability. The moderate durability against *C. puteana* is only for both treatments at 160 °C, but in other cases the experimental plywood can be classified as slightly durable. In this case, the tendency is completely different compared to the reference plywood. It should be concluded that the leaching or evaporation of thermal destruction products (and the leached amount) does not cause the same effect in all cases. If the removed destruction products themselves obviously favor the development of rot fungi for the reference plywood, then they have fungicide properties for the experimental plywood, and their removal even favors the development of fungi.

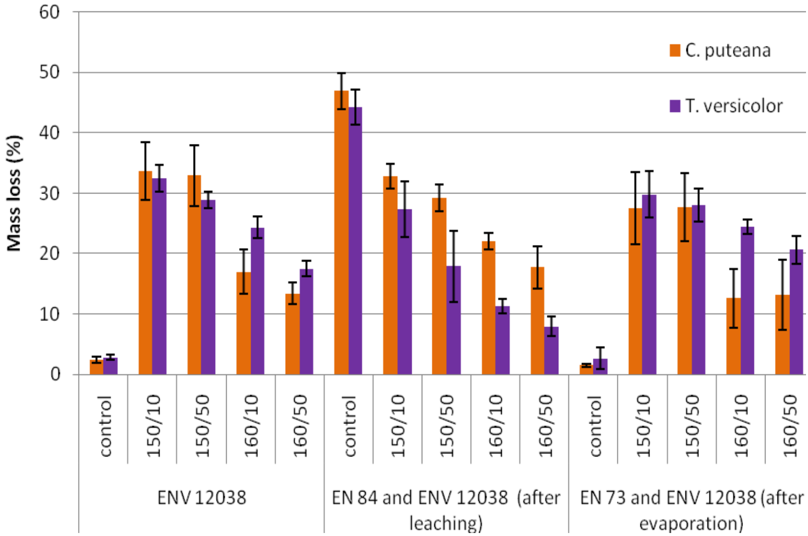

Fig. 17. Decay resistance – ML of experimental plywood after attack by the brown rot fungus *Coniophora puteana* and the white rot fungus *Trametes versicolor*.

It is important to evaluate the material biodurability not only in simulated laboratory conditions, but also in real outdoor conditions; therefore, plywood samples were placed in an outdoor test to determine the resistance against blue stain. Evaluating the biological overgrowing of the outdoor test samples, after the first month of exposure, no fungal staining was observed for the reference and experimental samples (Table 7) (rating 0).

After the second month, the reference plywood samples were more blue stained (>1) than the control (1). Experimental plywood control samples and at 150 °C THT samples were more blue stained (1–1.5) than the samples treated at 160 °C (0). After two months, the durability of the experimental samples against blue-stain was better (0–1.5) than for the reference samples (1–2). For the samples with non-covered edges, more intense development of blue-stain was observed on the exposed surface.

After three months of exposure, the reference plywood control samples and the THT samples reached the fungi staining rating of 3.8–4. The experimental samples showed better results – if the control and both THT regimes at 150 °C reached the colouring of 3.5–3.7, then the treatment at 160 °C, even partly, protected the material surface from blue-stain (2.7).

Table 7

Durability of Reference and Experimental Plywood against Blue Stain Fungi during 3 Months of Outdoor Exposure. Average Marks According to Rating 0–4

Time (month)	Control	Treatment temperature °C / time (min)			
		150/10	150/50	160/10	160/50
	Reference plywood				
1	0	0	0	0	0
2	1	2	2.0	1.8	1.2
3	3.8	4	4	3.8	3.8
	Experimental plywood				
1	0	0	0	0	0
2	1.2	1.5	1	0	0
3	3.7	3.5	3.7	2.7	2.7

As a result of THT, the plywood and also veneer surface change and become more hydrophobic. The greater surface hydrophobicity means that the water drop absorbtion into the wood is hampered, which is a positive property of the TM wood, if it is used in outdoor conditions. For the reference plywood, only the THT at 160 °C increases the surface hydrophobicity because the CA, compared to the case of the control plywood, grows by 18.6–20 % (Fig. 18). The treatment at 150 °C does not give any improvement, and CA is even by 3.8–9.8 % lower than that for the control.

For experimental plywood, the surface hydrophobicity is greater, and the CA for all samples is above 90°, which is significantly higher than that for untreated plywood. As a result of THT, the CA grows by 30.8–36.5 % at 150 °C and by 23.7–24.2 % at 160 °C. After 30 seconds CA of all the experimental samples remains above 90° (for the control – around 50°), but for reference samples it is only 45–60°.

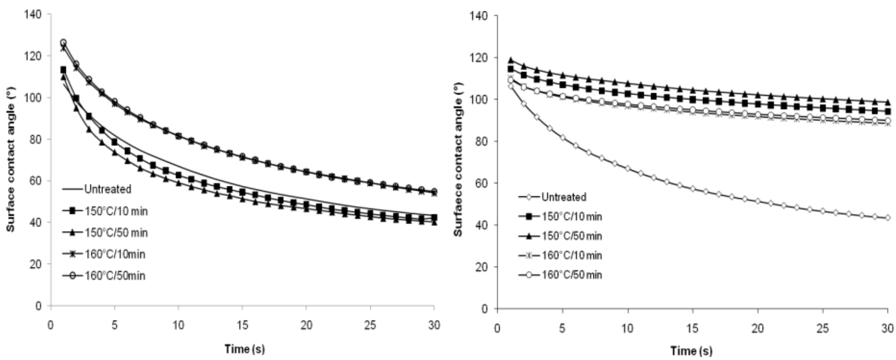

Fig. 18. Reference (left side) and experimental (right side) plywood surface contact angle during 30 second test period.

THT Plywood Prime Cost

A simplified calculation of the approximate cost of the plywood THT in a laboratory pilot plant was carried out. The plywood THT total cost is ~150 EUR at 150 °C and ~155 EUR at 160 °C (Table 8). The difference in cost between the regimes is minor and is formed on the basis of the labour cost.

Table 8

Total Costs of THT to Obtain 8.4 m^2 Plywood with 12 mm Thickness

Treatment temperature (°C) / time (min)	Material	Electricity	Labour	Water	Total (EUR)
150/10	68.04	5.48	76.3	0.13	149.95
150/50	68.04	5.99	76.3	0.13	150.46
160/10	68.04	6.08	80.93	0.13	155.18
160/50	68.04	6.18	80.93	0.13	155.28

From the data listed in Table 8, the calculated prime cost of the THT plywood with a thickness of 12 mm is 17.85–18.49 EUR/m^2. For plywood with a thickness of 12 mm (the price of 8.1 EUR/m^2 on the average) per 1 m^2, additional 9.75–10.39 EUR are required in the THT process. THT process added value exceeds 100 % of the raw material value.

Prime Cost of the Plywood Made from THT Veneer

A simplified calculation of the approximate cost of the veneer THT in a laboratory pilot plant and gluing with PF laminate to obtain the finished product was carried out. The cost of veneer THT and gluing to obtain the plywood is ~127 EUR at 150 °C and ~132 EUR at 160 °C (Table 9). The difference in cost between the regimes is small and is formed on the basis of the labor cost.

Table 9

Total Costs of THT and Bonding of Veneer to Obtain 5.25 m^2 Plywood with 11–12 mm Thickness

Treatment temperature (°C)/ time (min)	Material	Electricity	Labour	Water	Adhesive	Total (EUR)
150/10	36.11	5.13	84.39	0.12	1.58	127.33
150/50	36.11	5.46	84.39	0.12	1.58	127.66
160/10	36.11	5.76	89.02	0.12	1.58	132.59
160/50	36.11	5.99	89.02	0.12	1.58	132.82

The prime cost of the plywood glued from THT veneers (with a thickness of 11–12 mm) in 9 layers, calculated from the data listed in Table 9, is 24.25–25.29 EUR/m^2. To produce plywood from THT veneer, additional ~17–18 EUR/m^2 are needed. Thus, the added value exceeds 200 % from the raw material value.

In fact, the analogue for plywood obtained from the THT veneer is not normal, laminated or coloured plywood, but it can be considered a competitor to biocide impregnated plywood. In the world market, the price for impregnated plywood is ~ 113 EUR for a 2500 × 1220 × 18 mm plate or ~37 EUR/m^2 [10], which is considerably higher than the prime cost for our THT plywood and the plywood glued from the THT veneers. In addition, commercial impregnation autoclaves are used compared to the laboratory pilot equipment with low capacity as in our case.

Technological Scheme of Plywood THT Process

To obtain THT veneers and plywood, a plant with a technological scheme shown in Fig. 19 can be used. The main component of plant is stainless steel autoclave LV1. Necessary amount of material (veneer or plywood) is inserted through doors D. Water is filled in autocalve through valve N. Then open valves H and K and turn on pump P3, which pumps out air until the necessary vacuum is reached. Then turn off pump P3, close valve K and keep vacuum in system. LV2 is used as a tank, in which additional air pumped out from wood during vacuum process is collected. At the end of vacuum process, it is necessary to close valve H.

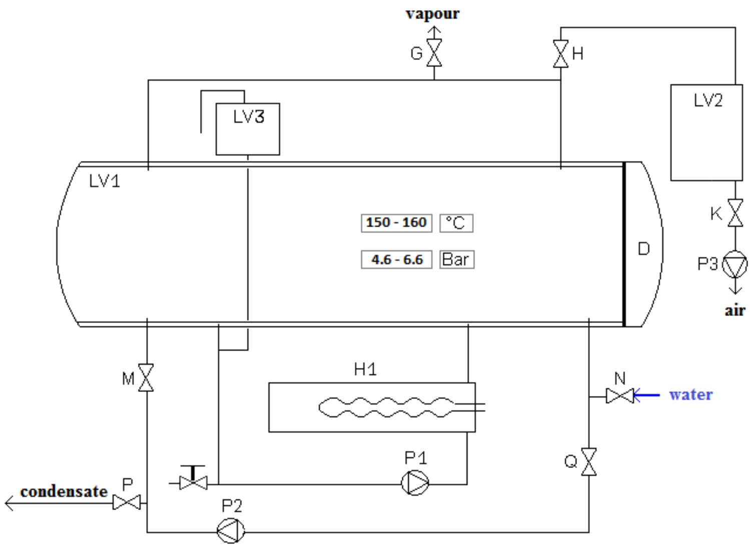

Fig. 19. Technological scheme of THT plant.

Then heating can be started, by turning on heating element H1, which is built in the tank with mineral oil. It is necessary to turn on pump P1, which ensures circulation of mineral oil in channels built in the autoclave wall. LV3 is a mineral oil thermal expansion tank. When the necessary temperature is reached, heating element H1 and pump P1 should be turned off. If temperature during the holding step decreases, heating sould be resumed to ensure the required temperature in the system.

After heating, the cooling step starts, which is performed by lowering the pressure in autoclave. Vapour generated during THT process is slowly blown out through valve G until normal atmosferic pressure in autoclave is reached. Then it is necessary to open valves M, Q and P and drain off condensate, which is generated during THT process. If solely by gravity the condensate is disrupted, it is necessary to close valve M and turn on pump P2 and deflate condensate from autoclave. Further cooling of autoclave is performed with lightly opened doors D. Material could be taken out when temperature does not exceed 35–40 °C.

CONCLUSIONS

1. In the THT process, chemical structure transformations occur in birch veneer wood, which cause the mass loss. The degree of polymerization of cellulose increases, a significant destruction of hemicelluloses occurs, and their destruction products are extracted with both acetone and water. As a result of the chemical component transformations, material elemental composition slightly changes, and the percentage of carbon increases and that of oxygen decreases.
2. The chemical transformations in THT veneer cause a whole range of changes in the properties. Veneer acquires a dark brown decorative color, and its surface and also the material itself become considerably more hydrophobic. The reduced tendency to absorb moisture and water favors the good durability of the THT veneer against staining fungi and slightly improves also the durability against rot fungi. Mechanical strength, especially tensile strength, significantly decreases for THT veneer, which is related to a significant destruction of hemicelluloses.
3. As a result of the THT process, the density of industrial birch plywood declines, there are mass losses, the surface acquires a dark brown decorative coloring, and cracks are formed on it. The THT plywood becomes more hydrophobic and absorbs considerably less moisture and water through both the surface and the whole volume. The THT plywood has improved durability against rot fungi after both leaching and evaporation, but THT does not give any improvement against discoloring fungi. As a result of THT, the adhesive is destroyed, which causes a significant reduction in bending strength and surface hardness. Both treatments at 160 °C impart better properties to plywood (except the mechanical and bonding strength) than at 150 °C.
4. The plywood glued from THT veneer has a dark brown decorative color, and its surface is smooth and hydrophobic. The material has reduced equilibrium moisture content and water uptake through the surface, and improved

dimensional stability. The mechanical strength (with the exception of bending strength) and gluing strength of such plywood decrease, but the improvement of biodurablity is negligible.

5. The veneer THT and further gluing with PF laminate are considered to be the most appropriate method for obtaining THT birch plywood, because the obtained product has more positive service properties.
6. The preferred veneer THT regime is 160 °C / 10 min and from it plywood is obtained with: increased density (+18 %); reduced equilibrium moisture content (−48 % to −52 %); enhanced anti-swelling efficiency (+36 %); reduced water uptake through the surface; reduced bonding strength (−21 % after 24H and −48 % after 4H+20H+4H pre-treatment); increased bending strength (+34 %); reduced surface hardness (−10 %); 3rd or 4th durability class against rot fungi; slightly enhanced durability against discoloring fungi.
7. The plywood made from THT veneer is classified according to the use class 3 (LVS EN 335) and is intended for use in outdoor and high humidity conditions, but due to the medium biodurability against rot fungi (3rd or 4th class according to CEN/TS 15083-1), subclass 3.1 is applicable to it that does not envisage the material long-term wetting, and water is not accumulated for a long time.
8. THT industrial birch plywood is recommended only for products for which the mechanical and bonding strength as well as surface condition after production are not important. In this case, both treatment regimes at 160 °C are suitable.

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