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RESISTANCE OF THERMALLY MODIFIED WOOD TO BASIDIOMYCETES*

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ABSTRACT

The object of the presented research project was sapwood of Scots pine (*Pinus sylvestris* L.), which was subjected to thermal and hydrothermal treatment. The objective of the performed investigations was to determine fungal resistance of this material to wood destroying fungi. Experimental wood was modified in the atmosphere of air and water vapour in conditions of the following temperatures: 160, 190 and 220°C for 6 and 24 hours. Fungal resistance of modified wood was determined applying an accelerated mycological test. The following test fungi were used in the performed experiment: *Coniophora puteana, Gleophyllum trabeum, Poria placenta* and *Coriolus versicolor*. The obtained results showed a correlation between conditions of the performed hydrothermal process of wood treatment and its resistance to test fungi species. Wood modified in the atmosphere of water vapour at the temperature of 220°C for 24 hours was characterised by the highest resistance against the selected organisms.

Key words: pine wood, thermal and hydrothermal treatment, biological resistance, fungal degradation, mycological test.

INTRODUCTION

Wood, as a biopolymer composite, has been known and recognised as construction material for a long time. Advantages of this material are appreciated very widely. However, considerable possibilities still remain associated with the improvement of wood natural quality characteristics such as dimensional stability or resistance to bio-corrosion, which might prolong the service life of wood products. In order to achieve these objectives, wood modification was developed as a method of equipping this material with new properties. Both wood physico-chemical characteristics and service properties depend on its chemical composition; first and foremost, on the presence of hydrophilic carbohydrate groups and their structure in cell walls. Increased resistance to the activity of biotic and abiotic agents as well as improvement of dimensional stability of wood can be achieved by the introduction of chemical compounds, which will either prevent the action of hydroxyl groups or exhibit activity toxic to wood decomposing organisms. However, both types of these compounds may pose a serious threat to the environment once the wood elements, which had been treated with such chemicals, are no longer necessary. Reduced wood hygroscopicity in the result of blocked hydroxyl groups should have a positive influence on selected wood service properties. Hydroxyl groups in carbohydrate wood constituents (cellulose and hemicelluloses) are reduced by heat application but it is important to remember that its upper limit should not exceed the level above, which the process of active pyrolysis begins (260°C). Results of experiments carried out by Madorsky [13] as well as by Shafizadeh and Bradbury [16] revealed that, at temperatures below 250°C, cellulose decomposition proceeded at low speed and the results of this process were H_2O, CO and CO_2 indicating that processes of dehydration and decarboxylation were taking place. In addition, in these conditions, the degree of cellulose polymerisation is reduced considerably but its reduction from 2600 to 600 does not result in weight loss [5]. Basch and Lewin [1, 2, 3] reported an increase in the extent of cellulose crystallinity heated in vacuum conditions at the temperature of 200°C. At temperatures below 200^{o}C, non-cellulosic carbohydrates, mono- and oligosaccharides and polysaccharides polymerise forming dextrins and branched polysaccharides. This process is accompanied, as in the case of cellulose, by liberation of H_2O, CO and CO_2. Lignin, which is considered as the most thermo-resistant wood constituent, undergoes slight decomposition already at the temperature below 200°C [14]. Hatekeyama [8] demonstrated that lignin undergoes softening at the temperature of 100-180°C.

The above-mentioned processes served as a basis for the development of a new method of wood modification by way of its multi-variant thermal treatment [4, 7, 11, 15, 17]. Experiments on the biological resistance of thermally modified wood were also undertaken at the Institute of Chemical Wood Technology of Poznań Agricultural University.

The objective of those investigations was to determine the impact of conditions of this process on wood resistance against white and brown rot fungal decomposition. The thermally modified wood might be widely utilised in the hazard class 3 as a wetherboard, cladding, siding, roof shingles, garden architecture, etc.

MATERIALS

Wood

Sapwood samples of Scots pine (*Pinus sylvestris* L.) measuring 50 x 15 x 5 mm (the last measurement along fibres) were used in the investigations. The experimental wood met all requirements to be fulfilled in the case of mycological research. Samples were stored in an air-conditioned area and the air-conditioning period lasted approximately 2 weeks. Mean wood absolute moisture content determined on a series of representative samples was about 12%, while its mean density determined at the above moisture content amounted to about 570 $kg*cm^{-3}$.

METHODS

Thermal treatment

Samples were placed on perforated shelves, which were fixed in a tight metal container equipped in connector pipes, which allowed introducing water vapour into it and disposing of steam-gaseous products of decomposition. The container was placed in a chamber furnace equipped in a control system allowing programming of the rate and time of heating. Thermal modification was carried out in the atmosphere of air and water vapour. The purpose of the application of water vapour was to remove products of hemicellulose hydrolysis from wood and, in so doing, depriving wood of products readily available for fungi. Experiments carried out in air atmosphere consisted in heating the container to the temperature of 110°C in 20 min and maintaining this temperature for 2 hours. Next, in the period of 60 minutes, the temperature inside the container was increased to the assumed soaking heating temperature. The assumed soaking heating temperatures were 160, 190 and 220°C and the times of thermal treatment at the above temperatures: 6 and 24 hours. In conditions of soaking heating in the atmosphere of water vapour, no intermediate treatment stage at the temperature of 110°C was applied. The container chamber was brought to the above-mentioned temperature levels while soaking heating times at these temperatures were also 6 and 24 hours.

Biological investigations

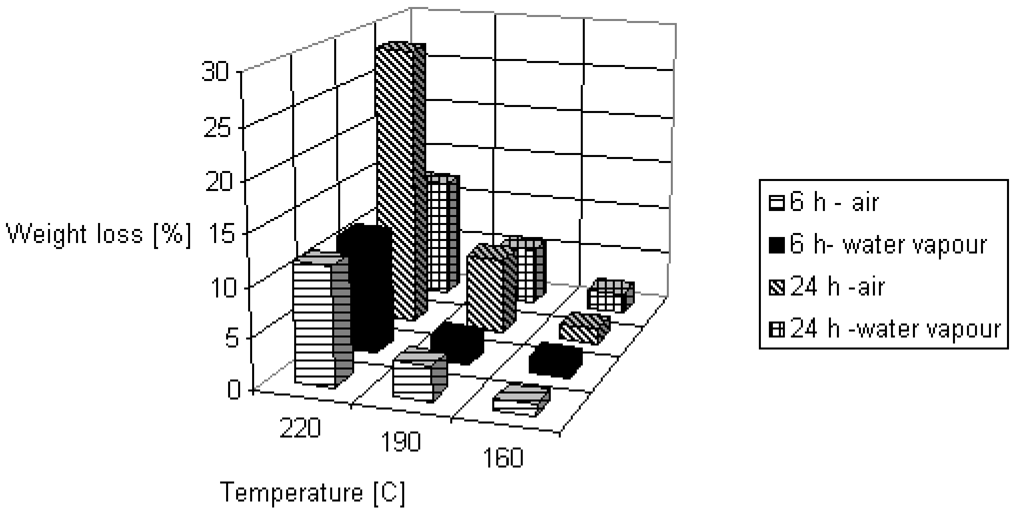
After thermal treatment, wood was subjected to investigations aiming to determine its resistance against selected species of fungi characteristic for white and brown rot. Mycological tests were carried out applying a rapid method based on recommendations found in the EN 113 standard. One technological variant of the obtained modified wood and tested fungus comprised the total of 8 samples. Five samples were used to calculate weight losses caused by the test fungi and three – to calculate correction coefficients. The period of the exposure to fungal action was 8 weeks. The following four fungal species were used in the described experiments: *Coniophora puteana* (Schum. ex. Fr.) Karst. strain BAM, Ebw. 15; *Coriolus versicolor* (L. ex Fr.) Quel. strain BAM Ebw. 214; *Gleophyllum trabeum* (Persoon ex Fries) Murrill strain BAM Ebw. 109; *Poria placenta* (Fr.) Cke. strain BAM Ebw 125.

RESULTS

Thermal treatment

The applied thermal wood treatment caused weight losses of samples, which increased with the increase of temperature and time of soaking heating as presented in Figure 1. Weight losses after 6-hour thermal treatment in air were comparable with the weight losses in water vapour atmospheres and increased from about 2% - at the temperature of 160°C to about 12% - at the temperature of 220°C. The dynamics of the sample weight losses increase subjected to soaking heating for 24 hours was considerably greater in the air atmosphere and weight losses increased respectively from 2% to over 28%, in comparison with samples subjected to the action of water vapour for which weight losses amounted to: 2.1% - at the temperature of 160°C, 5.9% - at 190°C and 12.4% - at 220°C. With the increase of sample weight losses, a decreasing darkening of wood was observed.

Figure 1. Mean weight loss of wood modified thermally in air and water vapour



Activity of test fungi

The measure of the activity of test fungi and, consequently, the indicator of the correctness of the performed investigations, was the weight loss of control samples (Table 1). The performed experiments showed high activity of brown rot fungi as weight losses attributed to their activity ranged in the interval of 23 to 46%. These values exceeded values of weight losses of control samples for individual fungi as minimal values required in the EN 113 standard. *C. versicolor* fungus was found to show smaller activity against natural wood probably because this species of fungus did not specialise in the decomposition of coniferous wood species. Weight losses at the level of only 15% could be attributed to the adjustment of this organism to the decomposition of wood of broad-leaved species. This fungus was used in the described experiments because of the prognosticated changes of lignin content in the modified wood in comparison with natural wood.

Table 1. Wood weight losses (WL, %) in the result of action of test fungi and wood moisture content (MC, %) in an agar-block test for control samples

Coniophora Puteana		Gleophyllum trabeum		Poria placenta		Coriolus vericolor	
WL	MC	WL	MC	WL	MC	WL	MC
39.4	81.0	23.5	100.4	45.8	53.6	15.4	69.6

Wood moisture content

After mycological tests, wood reached moisture content considerably exceeding the fibre saturation point for all variants of the mycological test (Table 1). The discussed values confirm advantageous conditions for the decomposition of modified wood in which these experiments were carried out.

Biological resistance of wood modified at the temperature of 160°C for the period of 6 hours

The observed resistance of experimental samples against the activity of test fungi was very low (Table 2). In the case of *P. placenta* and *C. versicolor* fungi, mean weight losses of modified samples were similar to those recorded in the case of weight losses of control samples. Samples of wood modified in air atmosphere and subjected to the activity of *C. puteana* and *G. trabeum* fungi exhibited weight losses by about 5% higher than those observed in the case of control samples. Moisture content in samples examined after the mycological test ranged from 75 to 140%, depending on the species of the tested fungus.

Table 2. Wood weight losses (WL, %) in the result of action of test fungi and wood moisture content (MC, %) in an agar-block test

Process parameters	Coniophora puteana		Gleophyllum trabeum		Poria placenta		Coriolus vericolor	
	WL	MC	WL	MC	WL	MC	WL	MC
160°C, 6h, air Control	40.6 35.3	74.8 76.5	18.9 15.3	125.0 122.2	42.3 42.9	78.1 74.7	12.6 12.8	77.4 90.9
160°C, 6h, water vapour Control	20.0 32.3	57.4 65.2	25.6 21.9	141.7 106.9	42.4 40.5	75.7 68.4	14.1 14.1	68.3 84.9
160°C, 24h, air Control	9.3 37.4	54.1 72.5	26.1 17.5	94.4 116.8	44.7 43.8	66.8 68.3	14.0 15.7	78.7 69.8
160°C, 24h, water vapour Control	26.4 31.2	57.9 67.4	23.6 14.6	104.1 136.1	46.5 48.3	63.1 65.0	12.2 12.6	68.4 69.0

Biological resistance of wood modified at the temperature of 160°C for the period of 24 hours

Following thermal treatment in the atmosphere of air, only samples subjected to the action of *C. puteana* fungus exhibited an increased fungal resistance (Table 2). Weight losses of the examined samples caused by the activity of this fungus amounted to about 9%, while the weight loss of control samples reached almost 40%. No improvement of wood fungal resistance was observed for the remaining variants within the examined technological parameters of thermal treatment. Moisture content of thermally modified wood, after the exposure to the action of test fungi, ranged from 54 to 104%.

Biological resistance of wood modified at the temperature of 190°C for the period of 6 hours

The above parameters of wood thermal treatment, both in the atmosphere of air and water vapour, increased wood resistance against the *C. puteana* fungus. Differences in weight losses of the examined experimental and control samples averaged 38% (Table 3). In the case of activities of the remaining test fungal species, no improvement in biological resistance was observed. Differences in weight losses ranged from 1.1 to 8.2%. Moisture contents of modified samples after the mycological examination ranged from 48 to 105%.

Table 3. Wood weight losses (WL, %) in the result of action of test fungi and wood moisture content (MC, %) in an agar-block test

Process parameters	Coniophora puteana		Gleophyllum trabeum		Poria placenta		Coriolus vericolor	
	WL	MC	WL	MC	WL	MC	WL	MC
190°C, 6h, air	5.9	48.1	11.3	94.2	42.7	63.8	8.5	80.1
Control	44.5	84.2	18.8	123.4	45.7	69.4	12.7	77.0
190°C, 6h, water vapour	7.0	49.0	18.0	104.8	42.1	67.4	7.7	72.0
Control	44.2	74.7	19.1	111.9	43.3	74.7	15.9	90.1
190°C, 24h, air	2.7	59.6	3.3	66.0	27.9	49.0	10.7	43.1
Control	45.4	74.1	18.5	135.1	46.9	67.0	11.5	80.6
190°C, 24h, water vapour	1.9	38.7	3.6	85.7	23.8	43.2	5.9	77.2
Control	38.8	72.4	15.6	134.0	46.8	75.6	10.9	81.1

Biological resistance of wood modified at the temperature of 190°C for the period of 24 hours

Thermal treatment of wood in this temperature, both in air and water vapour conditions, increased wood resistance against all species of tested fungi (Table 3). The greatest differences in weight losses of control and experimental samples were recorded in the case of activities of *C. puteana, G. trabeum* and *P. placenta* fungi. Differences in weight losses amounted to, respectively: 43, 15 and 19% - for samples modified in the atmosphere of air and to 37, 12 and 23% - for samples modified in the atmosphere of water vapour. The resistance of experimental samples against the *C. puteana* fungus was characterised by wood weight losses at the level of 2.7% (modification in air atmosphere) and 1.9% (modification in water vapour atmosphere). In the case of the remaining fungal species and both types of treatments, the respective values were: 3.3 and 3.6%; 27.9 and 23.8% and 10.7 and 5.9%. Wood moisture content after investigations ranged from 39 to 86%.

Biological resistance of wood modified at the temperature of 220°C for the period of 6 hours

After thermal treatment in the above-mentioned conditions, wood showed high resistance against the action of test fungi. Weight losses of samples modified in air and water vapour atmospheres subjected to the action of *C. puteana, G. trabeum, P. placenta* and *C. versicolor* fungi amounted to, respectively: 0.8 and 1.1; 2.5 and 1.8; 4.8 and 8.9 and 3.4 and 3.2%. Wood moisture content after experiments ranged from 34 to 81% (Table 4).

Table 4. Wood weight losses (WL, %) in the result of action of test fungi and wood moisture content (MC, %) in an agar-block test

Process parameters	Coniophora puteana		Gleophyllum trabeum		Poria placenta		Coriolus vericolor	
	WL	MC	WL	MC	WL	MC	WL	MC
220°C, 6h, air	0.8	65.0	2.5	74.8	4.8	33.8	3.4	68.5
Control	38.6	66.8	16.3	133.7	45.4	73.7	14.2	76.0
220°C, 6h, water vapour	1.1	43.8	1.8	81.2	8.9	39.1	3.2	57.7
Control	40.0	66.7	23.7	130.0	54.2	78.9	9.9	54.0
220°C, 24h, air	1.6	38.6	4.0	53.4	2.2	46.0	4.7	40.0
Control	41.2	80.3	13.7	140.5	50.9	72.7	10.9	78.5
220°C, 24h, water vapour	1.3	47.4	1.6	70.8	2.2	37.7	3.0	56.7
Control	39.8	70.6	22.0	148.0	48.5	72.3	11.6	99.2

Biological resistance of wood modified at the temperature of 220°C for the period of 24 hours

The most extreme process conditions of wood thermal treatment led to the highest losses of its weight, reaching 28% when wood was modified in air conditions and 12% in water vapour. Similarly to the previous technological variant, the applied thermal treatment parameters turned out to be equally effective from the point of view of increasing wood resistance against the action of test fungi. The smallest sample weight losses were found in the case of wood modified in conditions of water vapour (Table 4). The recorded weight losses were either smaller than or did not exceed 3%, which, in the case of testing the effectiveness of wood preservatives, is close to their limiting fungicidal value. Weight losses of samples subjected to the action of *C. puteana, G. trabeum, P. placenta* and *C. versicolor* fungi amounted to, respectively: 1.3; 1.6; 2.2 and 3.0%. Weight losses of samples modified in air and subjected to the action of fungi were slightly higher and amounted to: 1.6; 4.0; 2.2 and 4.7%. Wood moisture content after experiments ranged from 38 to 57%.

ANALYSIS OF RESULTS

Fungal resistance of thermally modified sapwood of the pine wood turned out to vary considerably. The extent of resistance to the action of test fungi, as expressed by the loss of wood weight caused by the action of a given test fungi, depended on the process conditions of the thermal treatment. Wood modified in air conditions in the temperature 160°C during 6h achieved by about 5% lower, in relation to non-modified wood, resistance against the action of *C. puteana* and *G. trabeum* fungi. The occurrence of this phenomenon can be attributed to a reduced extent of polymerisation of cellulose in a cell-wall during the process of thermal treatment. This was accompanied by a small wood weight loss which did nor exceed 2%. This can further be explained by polymerisation reactions, which accompany the break down on non-cellulosic carbohydrates in temperatures below 200°C. Sugar anhydrides, mono- and oligo- as well as polysaccharides polymerise at temperatures above 200°C forming dextrins as well as other branched carbohydrates. This kind of carbohydrate material can be more easily available for fungi [9]. Above the temperature of 200°C, hemicelluloses undergo rapid break down which is accompanied by the formation of a wide range of various dehydration products, volatile organic compounds, H_2O, CO and CO_2 and carbon substance. The main constituent of hemicelluloses is xylan or its glycuronic derivatives. Products of the decomposition of these compounds, e.g. furfural, can form toxic compounds affecting the resistance of wood to biodegradation caused by fungi. Kamdem et al. [12] maintain that increased resistance of wood modified at higher temperatures ca. 220°C is also affected by trace quantities of lignin phenol derivatives. This was confirmed by the high resistance of wood modified at the most extreme experimental temperatures (T = 220°C, t = 24 h) against the activity of the *C. puteana* fungus, which was characterised by the highest cellulolytic activity. The second most aggressive fungus with respect to its corrosive properties causing smaller weight losses of modified wood was the *C. versicolor* fungus. This organism is capable of breaking down, apart from carbohydrates, the lignin complex contained in the wood cell wall [6].

From the point of view of improving wood fungal resistance, the thermal treatment duration as well as conditions in which the process took place (air / water vapour) played a secondary role in comparison with the temperature parameter. Nevertheless, the application of water vapour allowed removing from wood products of hemicellulose hydrolysis as indicated by the smell of the steamed wood as well as the colour of condensates after wood hydrothermal treatment. In addition, this also confirmed the smallest weight losses in the result of the action of test fungi.

CONCLUSIONS

1. Wood modified in the environment of water vapour at the temperature of 220^{o}C for 24 hours achieved resistance against test fungi. The obtained resistance complied with the resistance of wood treated with the efficient chemical preservative.
2. Mild conditions of thermal treatment (160°C for 6 hours) increased the sensitivity of modified wood to decomposition caused by fungi used in the mycological test.
3. *C. puteana* and *C. versicolor* fungi, of all the applied test fungi, were found to be the most active towards thermally modified wood.

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