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Modification of wood with furfuryl alcohol catalysed by a mixture of acid anhydrides

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Abstract: The aim of this study was modification pine wood (*Pinus silvestris* L.) with furfuryl alcohol in the presence of mixture of succinic anhydride and maleic anhydride as catalyst. The modification of wood was conducted out in two steps. In first step wood was treatment with modifying mixture and then curing at 105 and 120°C. The use of acid anhydrides as catalysts in furfurylation process increases the values of the WPG and BC index and causes complete discoloration of the modified wood.

Keywords: wood modification, furfuryl alcohol, succinic anhydride, maleic anhydride

INTRODUCTION

The first process modification of wood with furfuryl alcohol, known as furfurylation process, were initiated by Alfred Stamm in 1950 (Hill 2006). One of the major problems with the furfurylation process has been the use of zinc chloride as a catalyst for the polymerization of furfuryl alcohol (FA). Zinc chloride used as a catalyst depolymerised the cellulose, which consequently reduced the strength of the modified wood. Schneider (1995) and Westin (1995) developed similar process with new catalysts based on cyclic carboxylic anhydrides. Positive results due to: a good solubility of catalysts in the FA without addition of water, similar the size of particles (molecules) and a similar degree of polymerization of at FA.

The properties of furfurylated wood depend on the retention of grafted/polymerized furfuryl alcohol in the wood. At the high modification levels the enhancement of wide variety of properties are achieved: an exceptional hardness increase, exceptional resistance to microbial decay and insect attack, high resistance to chemical degradation and high dimensional stability (Epmeier et al. 2004, Lande et al. 2004 a,b, Gobakken and Westin 2008, Esteves et al. 2011). The products of modification also have aesthetic appearance. The golden-brown colour is durable and resembles teak wood (Doczekalska et al. 2012).

The aim of this study was pine wood furfurylation with maleic and succinic anhydride as a catalyst. They were determined: the degree of modification products (determined the weight percentage gain (WPG) indicators), the depth of penetration of the modifier (W_D) and dimensional stability (bulking coefficient BC).

MATERIALS AND METHODS

Wood: Pine wood (*Pinus silvestris* L.) – dimensions 20 x 20 x 300 mm – air conditioned at a temperature of 20°C ± 2°C and humidity 60% ± 5%.

Wood modification with furfuryl alcohol: The process of modification of wood with furfuryl alcohol consisted of two main stages: impregnation and curing. The modifying mixture were consist of the following components: aqueous solution of furfuryl alcohol (FA) with concentration of 5 and 10% w/w of furfuryl alcohol or aqueous solution of furfuryl alcohol (FA) at concentrations of 5 and 10% with the addition of succinic anhydride (SA) and maleic anhydride (MA) in an amount of 4% or mixture succinic anhydride and maleic anhydride in an amount of 2% each. *Impregnation:* Impregnation of wood was carried out under reduced pressure (7 bar). The vacuum was maintained for 45 min. and then raised to atmospheric pressure and were maintained for a further 2 hours.

Curing: In the second step, the samples were cured for 3 hours at 70°C. Then wrapped them in aluminium foil. Curing of samples was performed at 105°C or 120°C for 12 hours.
Weight percent gain index (WPG): The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of samples before modification (W_1) and after modification (W_2) according to equation (1):

$$WPG = \frac{W_2 - W_1}{W_1} \cdot 100[\%] \quad (1)$$

Penetration depth is performed using the Brinell magnifying glass. The modified sample was cut in three places: in the middle of the length and 15 mm from each front. Using the Brinell magnifying glass measured with an accuracy of 0,1 mm penetration depth in location distant from each other about 5 mm. Index of diffusion (W_D) was calculated for each section and the average for whole sample according to equation (2):

$$W_D = \frac{P_P}{P_C} \quad (2)$$

where: P_P – discoloured cross-section area; P_C – the total cross-section area
Dimensional stability of the sample was determined using the bulking coefficient (BC), defined as follows:

$$BC = \frac{V_M - V_U}{V_U} \cdot 100[\%] \quad (3)$$

where: V_U – volume of the unmodified wood sample; V_M - volume of the modified wood sample.

RESULTS AND DISCUSSION

Table 1 presents the results of the determined percentage of the sample weight changes of the pine wood. WPG values differ depending on the composition of the impregnation mixture and the curing temperature.

The values of WPG for pine wood modified 5% of FA solution and curing at 105°C amounts to 16.8%. Addition of maleic anhydride to furfuryl alcohol, in an amount of 4%, caused a decrease WPG to about 14%. However, the WPG index for modified wood with 5% FA with 4% addition of succinic anhydride amounts to 28.2%.

Pine wood impregnated with 5% and 10% FA solutions and curing at 120°C has lower values WPG compared with pine wood after the impregnation and curing at 105°C. The lowest weight percent gain index was calculated for a sample of impregnated 5% FA without a catalyst. The addition of catalyst to the mixture of the modifying caused an increase in the WPG index of samples (table 1). The highest value WPG has a pine wood impregnated 5% FA with the addition of succinic anhydride.

Weight percent gain index of pine wood modified with 10% FA and curing at 105°C is 16.8%. The addition to the modifying mixture selected catalysts caused an increase in the WPG index of wood. Application to modification of pine wood mixture consisting of 10% FA and 4% succinic anhydride, resulted the highest value of WPG. A similar trend was observed for pine wood samples impregnated and cured at 120°C (table 1).

Table 2 shows the bulking coefficient (BC) of modified pine wood. The average values BC index obtained for all variants are in the range from 0.2 to 11.6% (table 2). The use of acid anhydride resulted in an increase in the BC index of modified pine wood. The highest BC index are calculated for the samples impregnated with 5% and 10% FA with the addition of succinic anhydride. For all the variants of modification was found to increase the curing temperature from 105°C to 120°C reduces the BC index.

Table 1. Weight percent gain index (WPG) [%] (average of 5 samples)

Composition of the modifying mixture	Temperature	
	105°C	**120°C**
5% FA	16.8 ± 4.9	1.8 ± 0.3
5% FA + 4% MA	14.8 ± 2.1	8.2 ± 1.0
5% FA + 4% SA	28.2 ± 1.6	13.2 ± 0.5
5% FA + 2%SA+2% MA	26.2 ± 4.6	10.3 ± 1.7
10% FA	16.8 ± 5.2	6.3 ± 0.7
10% FA +4% MA	21.2 ± 0.9	11.8 ± 2.2
10% FA + 4% SA	43.4 ± 4.2	14.4 ± 1.7
10% FA + 2%SA+2% MA	24.3 ± 5.2	20.6 ± 2.8

Table 2. Bulking coefficient (BC) [%] (average of 5 samples)

Composition of the modifying mixture	Temperature	
	105°C	**120°C**
5% FA	1.8 ± 1.1	0.2 ± 0.2
5% FA + 4% MA	3.2 ± 0.6	1.5 ± 0.4
5% FA + 4% SA	7.7 ± 0.5	4.0 ± 0.6
5% FA + 2%SA+2% MA	8.9 ± 1.0	2.4 ± 1.2
10% FA	4.0 ± 1.5	1.2 ± 0.4
10% FA + 4% MA	5.0 ± 0.5	2.8 ± 0.3
10% FA + 4% SA	11.6 ± 0.7	4.2 ± 0.5
10% FA + 2%SA+2% MA	6.5 ± 0.6	5.2 ± 0.8

Pine wood modified FA without catalysts and with the addition of one of the selected acid anhydride has an index of diffusion (W_D) equal to 1 (table 3). This W_D index value indicates that samples were discolored across their volume independently of compositions of impregnation mixture and curing temperature. Use in furfurylation process mixtures of catalysts (2% SA and 2% MA) reduced the W_D index.

Table 3. Index of diffusion (W_D)

Composition of the modifying mixture	Temperature	
	105°C	**120°C**
5% FA	1	1
5% FA + 4% MA	1	1
5% FA + 4% SA	1	1
5% FA + 2%SA+2% MA	0.95	0.93
10% FA	1	1
10% FA + 4% MA	1	1
10% FA + 4% SA	1	1
10% FA + 2%SA+2% MA	0.69	0.94

CONCLUSIONS

On the basis of research on modification of pine wood with furfuryl alcohol and acid anhydrides as a catalyst was found:

a) the value of the index WPG and index BC modified pine wood is influenced: concentration of furfuryl alcohol solution, the type of catalyst, curing temperature treated wood,
b) the best effect of the modification of pine wood with FA obtained using succinic anhydride as a catalyst,

c) use in the modification process furfuryl alcohol and furfuryl alcohol with succinic anhydride or maleic anhydride caused complete discoloration of samples as evidenced the value of W_D.

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Streszczenie: *Modyfikacja drewna alkoholem furfurylowym katalizowana mieszaniną bezwodników kwasowych.* Celem badań była modyfikacja drewna sosny (*Pinus silvestris* L.) alkoholem furfurylowym (FA) z zastosowaniem bezwodników kwasowych: maleinowego (MA) lub bursztynowego (SA) oraz mieszaniny tych bezwodników. Modyfikacja drewna była prowadzona w dwóch etapach. W pierwszym etapie drewno nasycano mieszaniną modyfikującą, w drugim wygrzewano w temperaturze 105°C i 120°C. Oceny stopnia modyfikacji drewna alkoholem furfurylowym dokonano na podstawie: wskaźnika procentowej zmiany masy (WPG), wskaźnika dyfuzji (W_D), współczynnika zmiany objętości (BC). Stwierdzono, że na wartość WPG i BC modyfikowanego drewna sosny wpływ mają: stężenie roztworu FA, rodzaj dodanego katalizatora oraz temperatura wygrzewania zaimpregnowanego drewna. Obecność wytypowanego katalizatora w roztworze impregnującym powoduje całkowite przebarwienie próbek drewna na co wskazują wartości wskaźnika dyfuzji (W_D). Najlepszy efekt modyfikacji drewna sosny uzyskano stosując jako katalizator procesu furfurylacji bezwodnik bursztynowy.

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