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Abstract European beech (*Fagus sylvatica* L.) is a major tree species of European forest which is underexploited because of its low dimensional stability and durability. Similarly to what has been developed with radiata pine, furfurylation might be the answer to optimize the utilization of local beech wood. Beech wood furfurylation process was studied using five different catalysts: maleic anhydride, maleic acid, citric acid, itaconic acid, and tartaric acid. Optimization of the furfurylation process was investigated for different catalyst and furfuryl alcohol (FA) contents, and different duration of polymerization. The following properties were studied: weight percent gain (WPG), leachability, anti-swelling efficiency (ASE), wettability, modulus of elasticity, modulus of rupture, Brinell hardness, and decay durability. Tartaric acid, never investigated up to now, was retained as catalyst to perform furfurylation due to its efficacy compared to other catalysts and its novelty. Wood modification with FA and tartaric acid as catalyst led to samples with high WPG even after leaching, improved ASE, and lower wettability with water. Increasing the polymerization duration increased the fixation of FA in treated wood. Most of all, treatment gave a significant improvement in mechanical properties and resistance to wood decaying fungi.

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Introduction

Wood has been used by mankind for millennia because of its interesting properties as raw material. Nevertheless, wood consists of natural polymers and it is susceptible to decay and moisture induced dimensional changes. Furthermore, competition with other building materials increases the need for high-quality wood-based products (Militz and Lande 2009). Traditionally, wood has been treated with biocides in order to prevent its degradation by wood rotting fungi, wood destroying insects, termites, and marine borers. However, these methods have become more and more controversial due to the use of chemical and poisonous substances as wood preservatives. The action of chemical, biological, or physical agent upon the wood material resulting in a desired property enhancement during the service life of wood has been defined as wood modification and proposed to replace the conventional wood preservation methods (Hill 2006). Epmeier et al. (2004) comparing properties of different wood modifications like acetylation, modification with methylated melamine formaldehyde, furfurylation, maleoylation, succination, and thermal modification in vegetable oil, found that furfurylation was one of the most effective modification among the others.

Modification of wood with furfuryl alcohol (FA), known as furfurylation, has been developed in the past several decades. FA is a derivative of furfural obtained through hydrogenation process. Furfural can be easily obtained from pentosans present in numerous agricultural by-products after acid hydrolysis and dehydration (Baysal et al. 2004). Polymerization of FA is generally carried out by using catalysts (organic acids, inorganic acids, and dehydrating agents) and high-temperature treatment (Wewerka 1968; Barr and Wallon 1971). Schneider (1995) investigated the properties of furfurylated sugar maple by using zinc chloride as catalyst on the basis of an initial study developed by Goldstein and Dreher (1960). Citric acid is one of the most studied catalyst in wood furfurylation (Lande et al. 2004b; Nordstierna et al. 2008; Venas and Rinnan 2008; Thygesen et al. 2010), followed by maleic anhydride (Nordstierna et al. 2008; Pfriem et al. 2012). Modification of wood using FA has been described to take place through different reactions (Lande et al. 2008): (1) homo-polymerization of FA, (2) co-polymerization and reactions with cell wall components, and (3) grafting of FA or poly(FA) to wood cell wall polymers. This statement has been confirmed by Nordstierna et al. (2008), who showed the formation of chemical bonds between lignin-like model molecules and poly(FA).

Furfurylation leads to an improvement of several wood properties. Esteves et al. (2011) reported that the furfurylation of wood can reduce the equilibrium moisture content (EMC) from 17.3 to 9 %. Baysal et al. (2004) found improvement in anti-swelling efficiency (ASE) and decrease in water absorption (WA) of furfurylated wood. FA has no or slightly positive effect on the mechanical properties (Xie et al. 2013). Some positive effects of mechanical properties are increase in modulus of rupture and elasticity (Lande et al. 2004b), and Brinell hardness (Epmeier et al. 2004). One of the drawbacks of this treatment is the decrease in the impact strength (Lande et al. 2004b). Durability is the most crucial aspect of the wood modification.

Furfurylation allowed improvement of durability against wood decaying fungi (Treu et al. 2009; Esteves et al. 2011; Li et al. 2015), termites (Hadi et al. 2005; Gascon-Garrido et al. 2013), marine borers (Westin et al. 2006), and weathering (Temiz et al. 2007). Furfurylated wood is reported to be not harmful for environment or users during and after service life, and even when burning, furfurylated wood did not release more VOC and PAH than untreated wood (Lande et al. 2004a; Pilgard et al. 2010).

Beech wood (*Fagus sylvatica*) is a major tree species of European forests (Silva 2010). However, according to EN 350-2 standard, beech is classified as a low natural durability species presenting high permeability and low dimensional stability. The aim of the study is to determine the optimal conditions for furfurylation of beech as to develop further industrial valorization of this underexploited species. For this purpose, nature of the catalyst, furfuryl alcohol content, and polymerization time were investigated to define better conditions for beech furfurylation, on the basis of different parameters like resistance of the treatment to leaching and improvement of treated wood properties characterized by measuring its decay durability, dimensional stability, mechanical properties, wettability, and dimensional stability.

Experimental

Sample preparation

All samples were prepared from the same beech (*Fagus sylvatica* L.) heartwood board presenting an average initial air dry density of 624 kg/m^3. Two kinds of wood specimens measuring $190 \times 100 \times 20$ mm^3 (*L, T, R*) and $190 \times 20 \times 20$ mm^3 (*L, T, R*) were prepared for impregnation of the different FA solutions and polymerization. After treatment, these specimens were used for further preparation of smaller samples necessary for characterization of different wood properties according to the procedure described in Fig. 1.
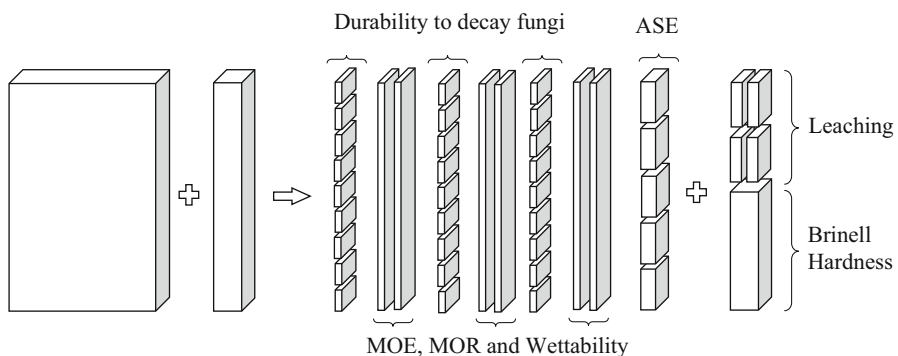
Fig. 1 Cutting method of wood specimens after polymerization process

$190 \times 20 \times 20$ mm^3 samples were used to prepare samples of $45 \times 20 \times 10$ mm^3 for leachability tests and samples of $90 \times 20 \times 20$ mm^3 for Brinell hardness test, while $190 \times 100 \times 20$ mm^3 were used to prepare samples of $30 \times 20 \times 10$ mm^3 for ASE tests, samples of $190 \times 20 \times 5$ mm^3 for mechanical tests (MOE, MOR), samples of $190 \times 20 \times 5$ mm^3 for wettability tests, and samples of $20 \times 20 \times 5$ mm^3 for durability tests. Initial weight of the samples was determined after oven drying for 48 h at 103 ± 1 °C.

Impregnation and polymerization

Impregnations were carried out in 3.5 L laboratory vacuum pressure reactor. Wood samples (one sample of $190 \times 100 \times 20$ mm^3 and one of $190 \times 20 \times 20$ mm^3) were introduced in the reactor. The reactor was closed and subjected to a vacuum of 1 mbar for 5 min followed by introduction of the aqueous FA solutions at different concentrations in the presence of different catalysts. Five catalysts used in this research were maleic anhydride (MA), maleic acid (MAc), citric acid (CAc), itaconic acid (IAc), and tartaric acid (TAc). After introduction of the impregnation solution, the reactor was subjected to a pressure of 12 bars for 5 min. The impregnated samples were then air-dried at room temperature for 48 h to evaporate the excess of water avoiding the appearance of cracks after polymerization. Samples were wrapped in aluminum foil to avoid furfuryl alcohol evaporation during curing and placed again in the reactor for polymerization. The reactor was closed and placed under nitrogen. The reactor temperature was slowly increased by 0.5 °C min^{-1} from ambient to 40 °C and maintained at this temperature for 10 h. After this period, the reactor temperature was increased by 0.5 °C min^{-1} from 40 to 120 °C and the temperature was maintained for different durations (6, 12, 18 or 24 h) according to the tested parameters. Heating was then stopped, and wood samples were allowed to cool down to room temperature under inert atmosphere.

Weight percent gain (WPG)

WPG due to chemical load was calculated from the following equation:

$$\text{WPG} = [(W_1 - W_0)/W_0] \times 100$$

where W_0 is the initial oven-dried weight (g) of the wood specimen before polymerization and W_1 is the final oven-dried weight of the polymerized wood specimen.

Leachability

Leaching test was performed by Soxhlet method for 6 h with water as solvent using two samples $45 \times 20 \times 10$ mm^3. Mass loss after leaching was calculated as follows:

$$WL = [(W_0 - W_L)/W_0] \times 100$$

where W_0 is the dry weight of wood sample before leaching (g) and W_L is the dry weight of wood sample after leaching.

Dimensional stability

Anti-swelling efficiency (ASE) was used to evaluate the dimensional stability of treated wood. The method, initially described by Rowell and Ellis (1978), was performed according to a procedure reported by Engonga et al. (1999, 2000). Three replicates of treated and untreated beech wood dried for 48 h at 103 ± 1 °C, cut into samples of $30 \times 20 \times 10$ mm^3, were measured according to their radial, longitudinal, and tangential directions to obtain the dry volume. Test blocks were soaked in water and then placed in a sealed desiccator to perform vacuum process for 1 h so that all of the wood cell wall filled with water. The samples were left submerged in water for 1 day, and then its volume was measured to obtain the wet volume. This process was repeated four times. Volumetric swelling of treated wood and untreated wood can be calculated with the following formula:

$$S_T = [(V_{WT} - V_{DT})/V_{DT}] \times 100$$

where S_T is swelling of treated wood, V_{WT} is wet volume of treated wood, and V_{DT} is dry volume of treated wood. Volumetric swelling of untreated wood and treated wood can be calculated with the following formula:

$$S_C = [(V_{WC} - V_{DC})/V_{DC}] \times 100$$

where S_C is swelling of untreated wood, V_{WC} is wet volume of untreated wood, and V_{DC} is dry volume of untreated wood. From the swelling difference between treated and control specimens, the ASE was calculated according to the following formula:

$$ASE = [(S_C - S_T)/S_C] \times 100$$

where S_C is volumetric swelling of untreated wood and S_T is volumetric swelling of treated wood.

Wettability

The measurement of contact angle was used to determine the wettability according to Engonga et al. (1999, 2000) methods. Contact angle of treated or non-treated wood was measured by optic method using a Krüss model FM40 easydrop goniometer at room temperature and humidity with water as the liquid. After programming the experimental conditions and adjusting baseline with the surface of beech wood, the measurement starts after water drops to the wood surface. There are three water drops for each treatment. For each drop, twenty measurements are performed automatically within three seconds time interval for one minute.

MOE and MOR

MOE and MOR were determined with samples of $190 \times 20 \times 5$ mm^3 according to EN 310 by a three point bending device INSTRON 4467 universal testing machine. MOE (N/mm^2) of each sample was calculated with the following formula:

$$E_m = \left[L^3(F_2 - F_1)\right]/\left[4bt^3(a_2 - a_1)\right]$$

where L is the distance between the centers of support in millimeters, b is the width of the sample in millimeters, t is the thickness of the sample in millimeters, $F_2 - F_1$ is the increase in load in Newton, on the cross section of the load-deformation curve, F_1 should be approximately 10 % and F_2 approximately 40 % of the breaking load, $a_2 - a_1$ is the shift of the arrow at mid-length of the test sample (corresponding to $F_2 - F_1$). MOR (N/mm^2) of each sample was calculated with the following formula:

$$f_m = (3F_{max}L)/(2bt^2)$$

where F_{max} is the breaking load in Newton. Six replicates were used for each treatment catalyst, content of catalyst, content of FA, and duration of polymerization.

Brinell hardness

This test was conducted according to EN 1534 on the test samples with a dimension of $90 \times 20 \times 20$ (L, T, R) mm^3. The test is performed on each of the tangential and radial faces of the specimens. The ball diameter is 10 mm; a force is applied gradually until its value reaches 1960 Newton in twenty seconds; this force is maintained thirty seconds, then slowly discharged. The measure of the depression allows the determination of Brinell hardness using the following formula:

$$HB = 2F\left/\left\{g \times \pi \times D \times \left[D - (D^2 - d^2)^{1/2}\right]\right\}\right.$$

where HB is Brinell hardness (N/mm^2), F is the nominal force (N), g is the acceleration of gravity (9.8 m/s^2), D is the ball diameter, and d is the diameter of the residual impression (mm).

Durability

Resistance to decay was evaluated by following a method derived from EN 113. In brief, white rot fungi *Coriolus versicolor* were inoculated on potato agar culture medium in petri dish and cultivated in an incubator at 22 ± 2 °C temperature and 70 ± 5 % of relative humidity for 7 days. After mycelium permeated the culture dish, three furfurylated or control wood samples were put in each petri dish and then placed in the incubator for another 16 weeks. Dimensions of the samples in this test were $20 \times 20 \times 5$ (L, T, R) mm^3 with 27 replicates for each treatment. The decay resistance was measured by weight loss according to the following equation:

$$WL = [(M_0 - M_1)/M_0] \times 100$$

where WL is the weight loss ratio (%) and M_0 and M_1 are dry weight of the samples before and after infection, respectively.

Durability class was determined according to EN 350-1 standard usually used to classify wood species natural durability. Samples were classified from very durable to not durable according to x value determined as follows:

x = WL of treated beech wood sample/WL of untreated beech wood sample

The different quotations are depicted in Table 1.

Statistical analysis

Statistical analysis of data based on the multi-step comparison Duncan method was performed using the SPSS 16 program. For each parameter measured, sample performance was studied versus applied treatment. Statistical analysis allowed classifying results into categories from A to D. Systems not connected by the same letter are significantly different at the 5 % level.

Results and discussion

WPG and leachability

Table 2 describes the effect of catalyst structure and concentration, of FA concentration and of curing conditions on the effectiveness of polymerization of FA into the wood as well as some wood properties like anti-swelling efficiency (ASE) and contact angle.

In all cases, polymerization of furfuryl alcohol, with or without catalyst, resulted in a significant improvement of wood dimensional stability and a decrease in wood surface wettability. According to the catalyst used, pH of the impregnation solution varied between 1.22 and 2.41, while pH of furfuryl alcohol solution alone was 4.10 allowing to catalyze polymerization of FA. PH of maleic anhydride and maleic acid solutions is quite similar indicating hydrolysis of anhydride function in water. Impregnation solutions prepared with MAc or MA showed the lower pH values due to the lower molecular weight of these two compounds leading to higher proton liberation. Weight percent gains (WPG) are directly connected to FA content used

Table 1 Natural durability classes of wood against decaying fungi based on EN 350-1

| Durability class	Quotation	Result of laboratory test
1	Very durable	$x \leq 0.15$
2	Durable	$x > 0.15 \leq 0.30$
3	Moderately durable	$x > 0.30 \leq 0.60$
4	Weakly durable	$x > 0.60 \leq 0.90$
5	Not durable	$x > 0.90$

Table 2 Weight percent gain (WPG), anti-swelling efficiency (ASE), leaching, and contact angle of beech wood sample subjected to different treatments of catalysts, furfuryl alcohol (FA), water, and duration of polymerization at 120 °C

Treatment	pH	WPG (%)	Leaching (%)	ASE (%)	Contact angle (°)	
					3 s	60 s
MA 5 %, FA 25 %, Water 70 %, 18 h	1.80	22.6 ± 2.6 C	7.5 ± 2.5 B	53.3 ± 0.5 C	41.2 ± 5.3	25.5 ± 8.6 B
MAc 5 %, FA 25 %, Water 70 %, 18 h	1.60	19.6 ± 1.1 AB	2.7 ± 1.4 A	42.3 ± 1.2 A	40.8 ± 7.7	29.0 ± 2.3 B
CAc 5 %, FA 25 %, Water 70 %, 18 h	2.29	19.4 ± 2.0 AB	4.3 ± 0.4 AB	50.2 ± 1.1 B	52.0 ± 6.7	33.3 ± 7.2 B
IAc 5 %, FA 25 %, Water 70 %, 18 h	2.41	16.1 ± 1.0 A	5.4 ± 0.3 AB	50.9 ± 1.5 BC	51.4 ± 9.3	24.3 ± 3.6 B
TAc 5 %, FA 25 %, Water 70 %, 18 h	2.11	25.2 ± 1.0 C	4.2 ± 1.6 AB	44.7 ± 2.7 A	55.6 ± 9.3	27.8 ± 3.6 B
MA 5 %, Water 95 %, 18 h	1.68	5.4 ± 0.1 D	10.9 ± 1.7 B	58.7 ± 0.8 C	38.3 ± 15.0	20.9 ± 8.7 BC
MAc 5 %, Water 95 %, 18 h	1.22	0.9 ± 0.3 A	10.3 ± 0.2 B	65.5 ± 5.7 C	32.9 ± 6.4	17.6 ± 1.3 BC
CAc 5 %, Water 95 %, 18 h	1.79	2.7 ± 0.5 B	3.3 ± 1.1 A	15.3 ± 3.3 A	52.9 ± 4.3	23.6 ± 2.7 C
IAc 5 %, Water 95 %, 18 h	2.09	3.8 ± 0.5 C	3.8 ± 0.3 A	27.6 ± 6.2 B	40.8 ± 4.3	17.6 ± 02.7 BC
TAc 5 %, Water 95 %, 18 h	1.76	2.9 ± 0.2 BC	4.2 ± 1.2 A	24.6 ± 1.3 B	36.5 ± 5.2	14.2 ± 0.9 AB
TAc 0 %, FA 25 %, Water 75 %, 18 h	4.01	9.7 ± 2.4 A	3.0 ± 0.2 A	36.6 ± 1.6 B	40.1 ± 1.6	22.6 ± 1.3 C
TAc 1 %, FA 25 %, Water 74 %, 18 h	2.39	13.4 ± 0.2 A	4.0 ± 0.9 A	22.1 ± 2.3 A	30.8 ± 6.7	17.2 ± 1.6 B
TAc 2.5 %, FA 25 %, Water 72.5 %, 18 h	1.99	17.8 ± 1.2 B	4.1 ± 0.9 A	40.2 ± 3.1 BC	37.3 ± 5.3	28.0 ± 3.2 D
TAc 25 %, FA 25 %, Water 70 %, 18 h	2.11	25.2 ± 1.0 C	4.2 ± 1.6 A	44.7 ± 2.7 C	55.6 ± 9.3	27.8 ± 3.6 D
TAc 5 %, Water 95 %, 18 h	1.76	2.9 ± 0.2 A	4.2 ± 1.2 A	24.6 ± 1.3 A	36.5 ± 5.2	14.2 ± 0.9 AB
TAc 5 %, FA 10 %, Water 85 %, 18 h	2.15	10.1 ± 1.2 B	5.8 ± 1.7 A	36.1 ± 2.8 B	28.9 ± 5.8	18.6 ± 4.5 B
TAc 5 %, FA 25 %, Water 70 %, 18 h	2.11	25.2 ± 1.0 C	4.2 ± 1.6 A	44.7 ± 2.7 C	55.6 ± 9.3	27.8 ± 3.5 C
TAc 5 %, FA 50 %, Water 45 %, 18 h	2.21	38.5 ± 3.2 D	5.3 ± 0.8 A	66.4 ± 0.8 D	43.8 ± 0.8	29.4 ± 2.2 C
TAc 5 %, FA 50 %, Water 45 %, 6 h	2.21	34.2 ± 1.6 A	5.0 ± 0.3 A	67.5 ± 0.2 A	42.6 ± 10.1	25.3 ± 2.0 B
TAc 5 %, FA 50 %, Water 45 %, 12 h	2.21	38.6 ± 3.0 A	3.4 ± 2.6 A	66.3 ± 1.1 A	44.3 ± 3.4	34.6 ± 1.8 B
TAc 5 %, FA 50 %, Water 45 %, 24 h	2.21	36.5 ± 2.9 A	2.2 ± 0.0 A	67.6 ± 1.3 A	43.3 ± 10.1	35.0 ± 2.0 B
Untreated	–	–	–	–	21.9 ± 4.5	9.0 ± 3.6 A

Values followed by the same letter do not differ significantly ($\alpha = 0.05$). Statistic analyses were carried out within the groups between lines in comparison with untreated sample which presents the same letter for all the groups in the case of this study
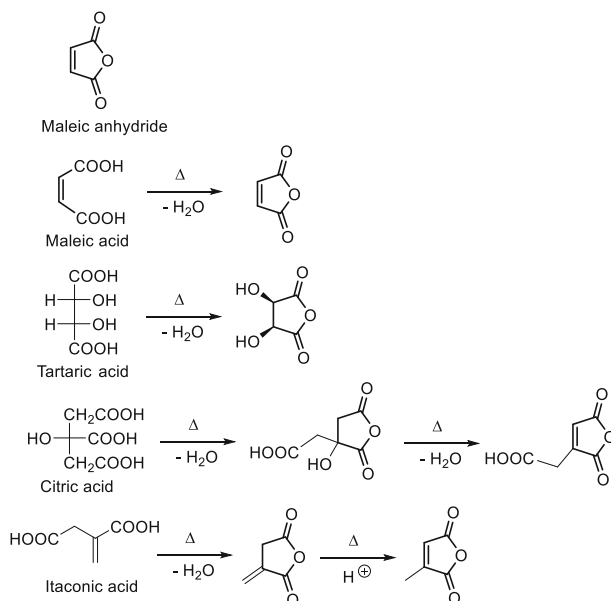
Fig. 2 Formation of reactive acid anhydride moiety resulting from dehydration of the butanedioic moiety present in the different catalysts

for impregnation. WPG are directly connected to the density increase observed with the increase in FA content in the impregnation solution. Structure of the catalyst influences directly the polymerization process of FA in the wood. WPG of furfurylated wood with 25 % of FA and 5 % of different catalysts are ranging from 16.1 to 25.2 %. Wood treated with tartaric acid presented the highest WPG followed by maleic anhydride, citric acid, maleic acid, and itaconic acid. Polymerization of furfuryl alcohol alone leads to lower WPG compared to polymerization performed in the presence of catalyst. At the same time, utilization of 5 % catalyst alone resulted in more or less important WPG according to the nature of catalyst, indicating that the latter ones do not behave only as catalysts but also react with wood explaining the weight gains observed. This behavior may be explained by the formation of acid anhydride (Fig. 2) resulting from dehydration of the butanedioic moiety present in each catalyst similarly to results reported by Ducoroy et al. (2007). These anhydrides are then able to react with hydroxyl groups of wood cell wall polymers explaining WPG obtained. At the same time, the presence of double bond or carboxylic acid function allowed reaction with furfuryl alcohol or its polymer through Diels–Alder reaction or esterification reaction explaining the higher weight gain obtained in the presence of catalyst and the better resistance of FA treatment to leaching (Gandini 2013).

Since tartaric acid permitted to obtain the highest WPG and had not been investigated before, the latter has been chosen for further optimization of the furfurylation process. WPG increased with catalyst and FA contents. The highest WPG was obtained from treatment with 50 % FA and 5 % tartaric acid catalyst

which resulted in a WPG of 40.7 % for larger sample. Li et al. (2015) reported similar WPG (41.8 %) on *Pinus massoniana* at the same content of FA catalyzed by oxalic acid mixed with citric acid. Meanwhile, Pfriem et al. (2012) obtained WPG of only 21.3 % for beech wood furfurylation using the same amount of FA catalyzed by maleic anhydride dissolved in ethanol solution. This comparison indicated that tartaric acid is a good alternative to other catalysts used up to now for polymerization of FA in wood. Leaching tests are used to evaluate the fixation of FA in wood during service. Maleic anhydride, used generally as common catalyst in furfurylation process, gives the highest weight loss followed by itaconic acid, citric acid, tartaric acid, and maleic acid. Leachability of polymer formed in wood varies according to catalyst and FA contents of impregnation solutions. Results reported by Lande et al. (2004b) and Treu et al. (2009) indicated that weight loss due to leaching decreased with increase in the WPG. Weight loss due to leaching decreased also with the increase in polymerization duration. According to these results, it can be concluded that 6 h of curing seems a good compromise in terms of cost due to treatment duration to ensure polymerization and fixation of FA into the wood, even if 24 h of polymerization will result in slightly better fixation. These results corroborated results obtained by Nordstierna et al. (2008) indicating that a longer reaction time and higher temperature increase the degree of polymerization of poly(FA) resulting in a better fixation in wood.

Dimensional stability

ASE ranges between 42 and 53 % independently of the catalyst using 25 % FA. Utilization of maleic anhydride permits to obtain the highest ASE followed by itaconic acid, citric acid, tartaric acid, and maleic acid. Even if ASE seems correlated with the quantity of FA used for the treatment, no direct relation was observed between WPG and ASE, when the same amount of FA was used varying the nature of catalyst. Impregnation solutions containing 50 % of FA permitted better dimensional stabilization of wood with ASE value of approximately 66 %. Pfriem et al. (2012) reported ASE value of 42 % for furfurylated beech wood presenting WPG of 33.9 %. According to statistical test, the increase in the tartaric acid and FA content will significantly affect the ASE, while the increase in duration of polymerization from 6 h to 24 h has no significant effect. The results here are consistent with those reported by Baysal et al. (2004) indicating that higher ASE value can be reached for higher WPG, bringing wood structure bulking and increasing its dimensional stability. Meanwhile, according to Lande et al. (2004b) there is a limit where further increase in WPG does not lead to a significantly higher dimensional stability. Improvement of dimensional stability in furfurylated wood can be explained by the polymerization inside the wood structure, in the lumen and in the cell walls, which prevents the water molecules to reach the wood polysaccharides, reducing thus equilibrium moisture content and increasing dimensional stability and durability (Esteves et al. 2011). Reticulation reaction between FA polymer, catalyst, and wood components may also explain the lower susceptibility of the material to bulking and its higher dimensional stability. More surprisingly, ASE values related to treatments performed with 5 % maleic acid or

anhydride without FA in water are extremely high, 65 and 59 %, respectively. This behavior may be explained by the ability of MAc or MA to crosslink with wood component hydroxyl groups explaining the high ASE values obtained (Li et al. 2012).

Wettability

Contact angles, surface free energy, and work of adhesion are the parameters generally used to define wettability (Walinder 2000; Bryne and Walinder 2010). Contact angles method was used in this study to investigate the wettability of furfurylated wood. There was an increase in contact angle value for all furfurylation treatments. Furfurylation using tartaric acid as catalyst leads to the highest contact angle after 3 s, 55.6°. This result is similar to that obtained by Bryne and Walinder (2010), who found contact angle of 56.7° for furfurylated wood using sessile drop method and water as test liquid. Increase in surface hydrophobicity may be an advantage for different wood utilizations, where water uptake may be harmful in order to avoid cracks or decay.

MOE and MOR

Table 3 shows MOE and MOR of furfurylated beech wood samples.

Furfurylation catalyzed with maleic anhydride, citric, itaconic, and tartaric acid increases the MOE of treated wood samples by about 20 % from 10,300 to 12,400 N/mm^2. Increase in MOE is even more pronounced in the case of the utilization of maleic acid as catalyst with an increase of 79.3 %, which may here be also associated with a higher reactivity of MAc with hydroxyl groups of wood cell wall polymers increasing internal strength of the material. The MOR of samples treated with tartaric, itaconic, and citric acid increased from 117 to 124 N/mm^2, maleic acid leading again to a higher increase up to 167 N/mm^2, while the MOR of sample treated with maleic anhydride decreased by 14.5 % from 117 to 100 N/mm^2.

The MOE of wood sample treated with 1 % of tartaric acid increased by 38.9 % from 10,300 to 14,307 N/mm^2, and the MOR increased by 13 % from 117 to 132 N/mm^2. Unexpected increase in MOE and MOR also occurred for sample treated with tartaric acid without FA. In this study, high levels of furfurylation significantly increased the MOE and slightly increased MOR. This result is confirmed by Lande et al. (2004b) who reported that the permanent bulking and grafting of FA polymer to the cell structure affect the stiffness, strength, and brittleness of the wood. However, Pfriem et al. (2012) found reduction in MOE in furfurylated beech wood catalyzed by maleic anhydride, while the other researchers concluded that MOE was not significantly changed by furfurylation (Epmeier et al. 2004, 2007; Esteves et al. 2011; Li et al. 2015).

Brinell hardness

The results of Brinell hardness test in different utilizations of catalysts are shown in Table 3. The highest Brinell hardness value was obtained for sample treated with

Table 3 MOE, MOR, Brinell hardness (BH), and density of beech wood sample subjected to different treatments of catalysts, furfuryl alcohol (FA), water, and duration of polymerization at 120 °C

Treatment	MOE (N/mm²)	MOR (N/mm²)	Brinell hardness (N/mm²)			Density (kg/m³)
			Rad	Tang	Mean	
MA 5 %, FA 25 %, Water 70 %, 18 h	12844 ± 1948 B	100 ± 19 A	4.7 ± 0.6	3.3 ± 0.2	4.0 ± 0.9 AB	787 ± 45 C
MAc 5 %, FA 25 %, Water 70 %, 18 h	18463 ± 2829 C	167 ± 23 C	4.7 ± 0.2	3.8 ± 0.3	4.2 ± 0.6 B	882 ± 43 D
CAc 5 %, FA 25 %, Water 70 %, 18 h	11652 ± 808 AB	121 ± 10 B	5.6 ± 0.1	5.1 ± 0.1	5.3 ± 0.3 C	679 ± 41 B
IAc 5 %, FA 25 %, Water 70 %, 18 h	11831 ± 501 AB	128 ± 5 B	3.5 ± 0.2	2.6 ± 0.2	3.1 ± 0.5 A	757 ± 69 C
TAc 5 %, FA 25 %, Water 70 %, 18 h	12422 ± 909 B	124 ± 11 B	6.2 ± 0.0	4.5 ± 0.1	5.3 ± 0.9 C	741 ± 33 C
TAc 0 %, FA 25 %, Water 75 %, 18 h	9905 ± 626 A	121 ± 5 AB	4.0 ± 0.2	3.7 ± 0.2	3.8 ± 0.2 AB	634 ± 20 A
TAc 1 %, FA 25 %, Water 74 %, 18 h	14307 ± 1434 C	132 ± 19 B	5.4 ± 0.1	4.5 ± 0.3	4.9 ± 0.6 BC	769 ± 25 C
TAc 2.5 %, FA 25 %, Water 72.5 %, 18 h	12532 ± 1129 B	109 ± 15 A	5.7 ± 0.5	4.7 ± 0.1	5.2 ± 0.6 C	728 ± 47 B
TAc 5 %, FA 25 %, Water 70 %, 18 h	12422 ± 909 B	124 ± 11 AB	6.2 ± 0.0	4.5 ± 0.1	5.3 ± 0.9 C	741 ± 33 BC
TAc 5 %, Water 95 %, 18 h	16809 ± 831 C	185 ± 8 D	3.1 ± 0.3	2.9 ± 0.1	3.0 ± 0.3 A	803 ± 18 D
TAc 5 %, FA 10 %, Water 85 %, 18 h	11692 ± 1410 B	98 ± 6 A	4.1 ± 0.4	3.9 ± 0.2	4.0 ± 0.3 B	667 ± 44 B
TAc 5 %, FA 25 %, Water 70 %, 18 h	12422 ± 909 B	124 ± 11 C	6.2 ± 0.0	4.5 ± 0.1	5.3 ± 0.9 C	741 ± 33 C
TAc 5 %, FA 50 %, Water 45 %, 18 h	12290 ± 658 B	109 ± 7 B	4.9 ± 0.0	4.0 ± 0.2	4.4 ± 0.5 B	758 ± 14 C
TAc 5 %, FA 50 %, Water 45 %, 6 h	11645 ± 335 B	107 ± 7 A	6.4 ± 0.5	5.4 ± 0.6	6.0 ± 0.7 D	772 ± 5 C
TAc 5 %, FA 50 %, Water 45 %, 12 h	12574 ± 592 C	112 ± 7 AB	4.5 ± 0.2	3.8 ± 0.4	4.1 ± 0.4 B	747 ± 8 B
TAc 5 %, FA 50 %, Water 45 %, 24 h	12741 ± 840 C	116 ± 8 AB	4.9 ± 0.1	4.3 ± 0.2	4.6 ± 0.4 C	765 ± 15 C
Untreated	10301 ± 569 AB	117 ± 5 B	3.9 ± 0.0	2.8 ± 0.2	3.3 ± 0.6 A	624 ± 3 A

Values followed by the same letter do not differ significantly ($\alpha = 0.05$). Statistic analyses were carried out within the groups between lines in comparison with untreated sample which presents the same letter for all the groups in the case of this study

5 % tartaric acid and 25 % FA increasing by 56.2 % from 3.9 to 6.2 N/mm^2 in radial section and by 55.4 % from 2.8 to 4.5 N/mm^2 in tangential section. Brinell hardness was also improved for samples treated with citric acid, maleic acid, and maleic anhydride, while samples treated with itaconic acid presented slightly lower hardness values.

The next part of Table 3 shows the Brinell hardness of treated sample at different content of catalyst. Brinell hardness increased with catalyst content. Increase in FA content will also increase the Brinell hardness value, treatment performed with 25 % of FA and 5 % of tartaric acid giving the highest increase in hardness. The sample treated with 5 % tartaric acid and 50 % FA during 6 h of polymerization presented the highest improvement of hardness, BH increasing by 62.2 % in radial direction and 91.8 % in tangential direction. Higher polymerization time resulted in lower value of BH, which remained, however, higher than those measured for control. According to statistical test, high level of furfurylation treatment significantly influences the Brinell hardness. Analogous results were reported by Lande et al. (2004b) and Esteves et al. (2011) showing that there was a clear increase in sapwood hardness in radial and tangential surfaces of about 50 %, BH increasing by about 20 % for 32 % WPG and 30 % for 47 % WPG. Epmeier et al. (2004) obtained a Brinell hardness increase of 100 % for furfurylated wood with 92 % WPG.

Durability

The resistance of the different furfurylated wood samples to the white rot decay fungus *Coriolus versicolor* is presented in Table 4.

Weight loss of furfurylated wood samples polymerized using different catalysts ranged between 8.9 % (tartaric acid) and 14.1 % (citric acid), while control samples presented weight losses of 39.1 %. According to EN 350-1, samples treated with 25 % of FA and 5 % of maleic anhydride, maleic acid, citric acid, and itaconic acid can be categorized in durability class 3 and those treated with tartaric acid in durability class 2. Treatment with 50 % of FA resulted in very low weight losses allowing efficient protection of all the treated samples.

At the same time, different duration of polymerization at high level of furfurylation did not affect significantly decay durability. FA concentration between 25 and 50 % is necessary to achieve efficient protection with WL of wood blocks inferior to 5 % justifying further experiments to evaluate the optimal FA concentration. According to the present results, beech wood furfurylated with 50 % of FA and 5 % of tartaric acid may be classified in durability class 1 (very durable). Treu et al. (2009) reported weight loss of 0.7 % for beech wood furfurylated with a WPG of 29.6 %, while untreated beech presented weight losses of 29.5 %. Furfurylation gives high protection against biodegradation (fungi, marine borers, and termites) at moderate and high level of modification. The penetration of resin into the wood cell wall or even cross-linkage reaction between FA and wood cell wall components changes the chemical nature of the cell wall, thus making it unattractive to decay fungi as shown by a clear decrease in mass loss due to fungal attack (Lande et al. 2004b, 2008; Esteves et al. 2011; Li et al. 2015). Nevertheless,

Table 4 Durability of beech wood sample subjected to different treatments of catalysts, furfuryl alcohol (FA), water, and duration of polymerization at 120 °C

Treatment	Weight loss (%)	Durability class (EN 350-1)
MA 5 %, FA 25 %, Water 70 %, 18 h	12.1 ± 2.4 B	3
MAc 5 %, FA 25 %, Water 70 %, 18 h	12.4 ± 3.5 B	3
CAc 5 %, FA 25 %, Water 70 %, 18 h	14.1 ± 8.1 C	3
IAc 5 %, FA 25 %, Water 70 %, 18 h	12.2 ± 5.2 B	3
TAc 5 %, FA 25 %, Water 70 %, 18 h	8.9 ± 2.6 A	2
TAc 0 %, FA 25 %, Water 75 %, 18 h	18.1 ± 11.7 B	3
TAc 1 %, FA 25 %, Water 74 %, 18 h	16.5 ± 5.2 B	3
TAc 2.5 %, FA 25 %, Water 72.5 %, 18 h	5.0 ± 1.3 A	1
TAc 5 %, FA 25 %, Water 70 %, 18 h	8.9 ± 2.6 A	2
TAc 5 %, Water 95 %, 18 h	14.4 ± 4.5 C	3
TAc 5 %, FA 10 %, Water 85 %, 18 h	9.0 ± 3.8 B	2
TAc 5 %, FA 25 %, Water 70 %, 18 h	8.9 ± 2.6 B	2
TAc 5 %, FA 50 %, Water 45 %, 18 h	2.7 ± 0.6 A	1
TAc 5 %, FA 50 %, Water 45 %, 6 h	3.4 ± 0.8 A	1
TAc 5 %, FA 50 %, Water 45 %, 12 h	3.2 ± 0.6 A	1
TAc 5 %, FA 50 %, Water 45 %, 24 h	3.5 ± 1.2 A	1
Untreated	39.1 ± 9.2 D	5

Values followed by the same letter do not differ significantly ($\alpha = 0.05$). Statistic analyses were carried out within the groups between lines in comparison with untreated sample which presents the same letter for all the groups in the case of this study

Pilgard and Alfredsen (2009) suggested that wood modification results in physical blocking of the entrance of decay and the reduction of equilibrium moisture content. It is more difficult for fungi to get the moisture required for decay. These hypotheses are consistent with the present results, blocks classified in durability class 1 presenting the higher contact angle values and consequently the lower wettability with water.

Conclusion

Furfurylation is a promising method to improve beech wood properties like dimensional stability, hydrophobicity, mechanical properties, and decay durability. Evaluation of different catalysts indicated that tartaric acid can be considered as a new promising catalyst to perform wood furfurylation. Further optimization of the furfurylation process by varying the quantity of catalyst, FA amount and polymerization duration allowed to define suitable conditions to enhance wood decay durability and dimensional stability. Duration of polymerization did not affect the WPG, but slightly increased the fixation of FA in the treated wood. Furfurylated wood becomes more hydrophobic independent of the nature of the catalyst used. Furfurylation increases MOE and Brinell hardness, while MOR was in general less

affected by the treatment. Even if the exact role of tartaric acid is not fully elucidated, it is postulated that tartaric acid does not behave only as an acidic catalyst but also as a reactant able to react with wood components allowing also fixation of FA polymer. Further studies will be necessary to investigate reactivity of tartaric acid with wood and its effect on FA polymerization.

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