Furfuryl Alcohol Treatment of Bamboo Betung (*Dendrocalamus asper* Backer ex K. Heyne) Strips

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Abstract

Based upon successful chemical modification of wood, bamboo strips were subjected to furfurylation treatment. Furfurylation in the mean of impregnating furfuryl alcohol to the bamboo and then heated at 100°C for 24 hours to produce solid polymeric resin. The success of furfurylation is assessed by uptake and the weight percentage gain of furfurylated bamboo strips. However, the treatability of dry bamboo strip is relatively poor. This paper studies the furfurylation process of bamboo betung (*Dendrocalamus asper* Backer ex K.Heyne) strips by soaking, vacuuming and the combinations thereof. Results showed that soaking bamboo strips for two days after vacuum treatment achieved optimum uptake of furfuryl alcohol solutions and gave rise to an 80% weight gain. Catalyst addition during furfurylation did not increase the weight percent gain. Water was an active solvent carrier for achieving higher weight gains.

Keywords: Bamboo strips, furfurylation, uptake, percentage weight gain, catalyst.

Introduction

Bamboo is a woody, valuable and robust material. It grows naturally on all continents except Europe (Liese 1987) and shows potential as a wood substitute given that its physical and mechanical properties are comparable with those of wood. The most significant advantage of bamboo is its growth rate. Bamboo grows up to 30 meters within six months in some tropical countries, demonstrating the potential of substituting bamboo for slower-growing wood species to increase annual yield (Liese 1987). Additionally, the extensive root network makes bamboo as a strong carbon fixate, erosion controller and water table preserver. Bamboo is an essential means of establishing reforestation and often has a positive effect on groundwater levels and soil improvement via the nutrients in its debris (van der Lugt *et al.* 2009).

Bamboo species are of enormous importance to rural people in several regions of Asia. For many centuries bamboo has played an essential role in the daily life of the people of tropical countries (Sharma 1980; Jifan 1985). Traditionally it is used for light building materials, scaffolding, ladders, mats, baskets, containers, tool handles, pipes, fencing, handicrafts, toys and musical instruments. In addition to traditional applications, modern processing techniques have considerably extended its usefulness in applications such as ply bamboo, bamboo mat board and laminated bamboo for flooring (Recht and Wetterwald 1992; Nugroho and Ando 2001).

Despite its many advantageous properties, bamboo is liable to attack by brown rot, white rot and soft rot fungi and by insects such as beetles and termites (Liese 1959; Kumar *et al.* 1994). Non-treated bamboo has an average life of fewer than 1~3 years when exposed to the atmosphere and soil. When used indoors, bamboo may be expected to last 4~7 years (Liese 1980), and therefore treatment is regarded as a necessity (Farelly 1984).

Environmental concerns regarding the use of chemicals for wood preservation has generated interest in alternatives such as chemical modification (Hill 2006). Wood modification is a means of altering the material to overcome one or more of its disadvantages. One of the chemical modification processes for wood is furfurylation (Jones 2007). Furfurylation is based upon the reaction of wood with the bio-chemical furfuryl alcohol at the cell wall level. The processes have significantly improved wood properties, protecting against decay, decreased hygroscopicity and improved dimensional stability (Jones and Hill 2007). Modification of wood with furfuryl alcohol resin is known to be an efficient method of obtaining wood products with high dimensional stability, high durability and resistance to alkali and acids (Homan and Jorissen 2004).

Furfuryl alcohol was first used to treat wood by Goldstein (1955), who impregnated wood with a mixture of furfuryl alcohol, water and a suitable acid catalyst. The impregnated wood was then heated at 100ºC for 24 hours to produce a solid polymeric resin. Goldstein (1955) demonstrated that zinc chloride and organic acids such as citric acid are suitable catalysts for furfurylation. Prior to curing, wood specimens were wrapped in aluminium foil and allowed to equilibrate for a day to enable migration of the solution through the structure by capillary action and diffusion (Goldstein 1955).

Furan derivatives are necessary industrial and manufacturing chemicals. They are used as solvents, reagents for chemical synthesis and as monomers in polymerization (Kim *et al.* 1998). The two intermediates employed for the commercial manufacture of furan resin are furfural and furfuryl alcohol. Furfural is produced from renewable agricultural by-products, and furfuryl alcohol is manufactured from furfural by a simple hydrogenation process (Schultz 1990). Furfuryl alcohol is the most important derivative of furan and is primarily used in the synthesis of adhesive polymers (McKillip and Sherman 1980). Furfuryl alcohol is a monomer of oligomeric furfuryl alcohol resins and is widely used as a highly durable thermosetting metal coating (Kim *et al.* 1998).

Furfuryl alcohol has a boiling point of 170°C and a molecular weight of 98.10. It is a colourless to golden clear liquid with a pungent smell that darkens rapidly in the presence of air due to oxidation. Furfuryl alcohol is produced by a partial reduction of furfural, which is derived from pentose (C_5 sugars) containing plant material. Currently, furfuryl alcohol is produced from sugar cane bagasse, corn cobs, oat hulls, rice hulls, straw and wood waste.

Furfuryl alcohol has numerous industrial applications and is used extensively as a selective solvent for lubrication oil refining and extraction of unsaturated C_4 and C_5 hydrocarbons. It is widely used in foundries and the manufacture of anticorrosive paints. Furfuryl alcohol has been used for the preparation of materials requiring stability, acid, alkali and solvent resistance at relatively low costs. Some of the elements that have been manufactured using furfuryl alcohol resin include tabletops, ceramic sinks, furfuryl alcohol resin cement for bonding corrosion-resistant tiles or bricks, tank coatings, brick linings, bonding of glass fibre mats, adhesives in aircraft industries, manufacture of storage battery cases, solvent for cellulose esters, vinyl compounds, many natural gums and phenolic resins (Schmitt 1974).

Furfurylation with or without catalyst has been reported to enhance several properties of wood, such as protection against decay (as a result of reduced moisture and altered wood chemistry), increased dimensional stability (as a result of polymerization in the cell lumens), golden brown appearance and decreased hygroscopicity (Jones and Hill 2007). For wood, various treatment methods have been studied for furfuryl alcohol impregnation, including the full cell (Bethell) and empty cell (Lowry) processes (Goldstein 1955). Several different catalysts have been tested for the use with furfuryl alcohol. Goldstein and Dreher (1960) examined numerous catalysts and found a small number to have the potential use (zinc chloride, maleic acid, malonic acid, tartaric acid, malic acid and citric acid). Catalyst concentration of 5% was determined as sufficient for wood furfurylation.

Wood treated with furfuryl alcohol requires curing. This involves placing the samples in a uniformly heated environment for a set period. Curing time for furfurylation can be defined by three steps: polymerization of the alcohol resin, early resin curing stage (rubber) and slow curing stage (brittle). The initial moisture content of wood also affects the furfurylation process in wood. Schultz (1990) suggested that the water content of the cell walls has an effect upon the process.

Furfurylation has not been investigated as a possible treatment of bamboo. Recommended methods for liquid penetration of bamboo include soaking and vacuum with less pressure (Kumar *et al.* 1994). Vascular bundles which contain meta-xylem vessels and thickly walled fibre play an essential role in liquid penetration in bamboo. Unlike wood, there are no ray cells in bamboo, and the horizontal movement of liquid from vessels into neighbouring parenchyma tissue and fibres is by diffusion (Liese 1980). The diffusivity of furfuryl alcohol may facilitate the movement of the chemical from the lumens in vessels into surrounding tissues. This paper examines the possible applicability of furfurylation to bamboo strips.

Materials and Methods

Furfuryl Alcohol Treatment of Bamboo Strips

Strips of bamboo betung (*Dendrocalamus asper* Backer ex K. Heyne) were prepared from the outer, middle and inner regions of culm wall. Strips with the dimension of 5 x 10 x 75 mm were prepared free from inner and outer layers. Ninety strips were grouped into three treatments (soaking, vacuum and vacuum followed by soaking) and three regions (outer, middle and inner), each with ten replicates. To avoid bias, matched samples were prepared from one internode of ten bamboo culms.

After weighing, the strips were treated using 95% furfuryl alcohol by soaking, vacuum and a combination of vacuum and soaking. The soaking time was 1, 2, 3, 4 and 5 days. The vacuum method was applied by loading the strips in a vacuum glass container and evacuated in -85 kPa (gauge) for 10, 15 and 30 minutes before flooding with the 95% furfuryl alcohol. For the combination method, strips were evacuated for 10 minutes followed by soaking in solution for 1, 2, 3, 4 and 5 days.

The Effect of Catalyst and Carrier upon Furfurylation

Bamboo betung (*Dendrocalamus asper* Backer ex K. Heyne) blocks (10 x 10 x 10 mm) were prepared from one internode of bamboo culm (Fig. 1) to avoid bias. Two tropical hardwood species (*Anthocephalus chinensis* and *Calophyllum* sp.) with a slightly lower and higher density than bamboo were subjected to an identical process for comparison. All samples were oven-dried to allow calculation of the initial weight of non-modified blocks prior to treatment with furfuryl alcohol.

All blocks were treated using vacuum (-85 kPa) for 10 minutes, followed by two days soaking in a mixture of furfuryl alcohol and catalyst. A mixture of 90% furfuryl alcohol, 5% water, and 5% catalyst was combined on a weight/weight basis for the 5% catalyst loading solution. Catalysts used in this study included citric acid, zinc chloride, and maleic acid.

To determine the effectiveness of the ratio of water: furfuryl alcohol for bamboo furfurylation, four solutions of water and furfuryl alcohol (90:10; 50:50; 30:70; 15:85) were examined. Eight replicates were employed for each treatment. After treatment, all samples were wrapped in aluminium foil and cured in an oven at 103ºC for 16 hours. The aluminium foil was then removed, and the specimens were post-cured for further eight hours at 103ºC. All surfaces of the blocks were sanded slightly in order to avoid the effect of poly-furfuryl alcohol coating (Westin *et al.* 2004). A critical parameter of furfurylation is the polymer mass after curing (Venas and Rinnan 2008). The polymer mass was evaluated by the weight percent gain.

Results and Discussion

Furfuryl Alcohol Treatment of Bamboo Strips

The average furfuryl alcohol uptake with soaking time is shown in Table 1. Generally, the average liquid uptake increased with increasing soaking time. Strips taken from the middle region achieved an average uptake of 24.1 kg/m^3 after one day, followed by 28.9 kg/m^3 after a further day. The highest uptake reached 34.3 kg/m^3 was achieved after five days of soaking.

Bamboo strips taken from the outer regions of the culm wall achieved higher uptake than the middle and inner strips. Strips taken from the outer region achieved an average uptake of 25.9 kg/m^3 after one day, followed by 31 kg/m^3 after two days and reached an uptake of 40.8 kg/m^3 after five days soaking. Two-way analysis of variance showed soaking time (1~5 days soaking) was significantly different (F = 161.5, p = <0.001) and similarly, strip portion (outer, middle and inner) was significantly different (F = 190.4, p = <0.001). The furfuryl alcohol uptake was rapid on the first day, followed by a slight uptake increase with subsequent soaking. The rapid initial uptake presumably occurred by capillary flow through vessels.

Furfuryl alcohol uptake after soaking varied between strips (outer, middle and inner). The outer strips demonstrated the highest uptake, while the inner strips had the lowest uptake. It is postulated that liquid penetrates mainly through vessels which more frequently exist in the outer region than the middle and inner sections (Liese 1980). The average furfuryl alcohol uptake after vacuum treatment is shown in Table 2.

Table 1. Furfuryl alcohol uptake of bamboo strips after soaking.

Bamboo Strips	Soaking time									
	1 day		2 days		3 days		4 days		5 days	
	x	*sd*	*x*	*sd*	*x*	*sd*	*x*	*sd*	*x*	*sd*
Outer	25.99	1.44	31.01	1.26	35.41	1.52	39.16	2.24	40.81	2.58
Middle	24.14	1.30	28.85	1.78	31.84	2.34	33.39	1.83	34.32	2.21
Inner	20.31	1.85	23.08	0.85	26.35	1.51	28.47	1.36	29.87	1.88

Remarks: *x*=mean; *sd*=standard deviation.

Table 2. Furfuryl alcohol uptake in bamboo strips after vacuum treatment.

Bamboo Strips	Vacuum time							
	10 minutes		15 minutes		20 minutes		30 minutes	
	x	*sd*	*x*	*sd*	*x*	*sd*	*x*	*sd*
Outer	113.42	2.69	126.45	4.23	121.51	2.42	122.72	2.78
Middle	107.30	3.12	110.14	4.42	119.72	2.10	116.27	2.33
Inner	92.49	1.07	89.53	1.84	90.67	1.25	93.59	1.37

Remarks: *x*=mean; *sd*=standard deviation.

Table 3. Furfuryl alcohol uptake in bamboo strips after an initial vacuum followed by soaking.

Bamboo Strips	Soaking time											
	0 day		1 day		2 days		3 days		4 days		5 days	
	x	*sd*	*x*	*sd*	*x*	*sd*	*x*	*sd*	*x*	*sd*	*x*	*sd*
Outer	118.1	5.9	121.9	3.2	131.9	2.2	134.2	2.4	134.9	2.9	135.9	2.8
Middle	106.1	3.6	118.3	4.7	134.9	1.1	137.3	2.2	140.5	1.4	141.9	1.4
Inner	93.5	1.8	104.1	4.5	116.4	3.6	117.9	3.2	119.8	3.1	120.6	3.1

Remarks: *x*=mean; *sd*=standard deviation.

Liquid uptake of bamboo strips after vacuum treatment was substantially higher than that achieved by soaking. The average uptake of strips vacuum treated was about three times higher than those soaked. The average uptake of the middle strips was 107.3 kg/m^3 with vacuum treatment compared to 34.3 kg/m^3 after five days soaking. In the culm, there are air bubbles that restrict the entry of solution. A vacuum condition was able to remove these air bubbles and allow higher uptake partially. The liquid uptake in bamboo strips slightly increased with increased vacuuming time. Two-way analysis of variance showed vacuuming time (10~30 minutes) was significantly different (F = 37.6, p = <0.001) and similarly, strip portion (outer, middle and inner) was also significantly different (F = 1305.6, p = <0.001). Strips from the inner region of the culm gain less liquid than the outer and middle regions. This is attributed to the smaller number of vessels found in the inner section.

The average furfuryl alcohol uptake in bamboo strips after an initial vacuum followed by soaking is shown in Table 3. Liquid uptake of bamboo strips after an initial vacuum followed by soaking treatment was considerably higher than that achieved by soaking and vacuuming alone. The average uptake of middle strips was 141.9 kg/m^3 after 10 minutes vacuuming followed by five days soaking, compared to only 34.3 kg/m^3 uptake after five days soaking only. The uptake improvement after vacuuming and soaking treatment is presumably caused by liquid penetrating through vessels during vacuuming followed by solution moving into the surrounding vessels by diffusion.

The results revealed that two days soaking after vacuum treatment achieved an optimum level of uptake in the bamboo strips. This confirms the findings of Skewes (2004), who reported that wood containing furfuryl alcohol continues to swell for up to 48 hours. Furfuryl alcohol expanded in the bamboo cell wall, allowing more liquid penetration.

Two-way analysis of variance showed soaking time after vacuum treatment (0~5 days) was significantly different (F = 290.58, p = <0.001) and similarly, strip portion (outer, middle and inner) was also significantly different (F = 432.4, p = <0.001).

The Effect of Catalyst and Carrier Upon Furfurylation

The average weight percent gain of sample blocks after furfurylation is shown in Fig. 1. The graph in Fig. 1 shows bamboo block samples with catalyst addition gained less weight than without catalyst. Two tropical hardwoods increased various weight percentage with catalyst addition. *Anthocephalus* woodblocks, which were less dense than bamboo, gained up to 142% weight after furfurylation with maleic acid as a catalyst. The high percentage gain (more than 100%) is due to polymerization of furfuryl alcohol not only in the wood cell wall but also in the void volume between cells. *Calophyllum* woodblocks which were denser than bamboo gained 87.4% weight with maleic acid addition. In hardwood block samples, the use of maleic acid as a catalyst achieved the highest percentage gain.

Bamboo blocks gained 2~3% weight after furfurylation with the catalyst. Visual investigation showed dark solution lying upon the surface of the blocks (Fig. 2A). The blocks cross-sections were filled with a coloured solution, but the surrounding ground parenchyma tissue appeared clear from the solution (Fig. 2B). Furfuryl alcohol solutions with catalyst addition did not penetrate the bamboo blocks, due to premature polymerization of furfuryl alcohol blocking further penetration of the solution.

Visual examination of furfurylated blocks shows dark cured resin appearing not only in the vessels but also in the ground parenchyma tissue (Fig. 2). Water solvent carrier improved the diffusion rate, and as a result, the furfuryl alcohol penetrated more area of the bamboo blocks.

The average weight percent gain of sample blocks after furfurylation with different concentrations is shown in graph Fig. 3. The furfuryl alcohol mixed with water resulted in considerably increased weight percent gain in bamboo blocks. Bamboo blocks treated with 90% furfuryl alcohol gained the highest weight percentage (up to 84%). Weight gain decreased with lower furfuryl alcohol concentration. This trend was not noted in the hardwood blocks. In hardwood blocks, furfurylation without catalyst resulted in lower weight percentage gain. The higher weight gained by bamboo blocks is possibly due to more significant starch content in bamboo. The starch is decomposed by the heat during curing, creating an acidic environment which accelerates furfurylation.

Visual examination of furfurylated blocks shows dark cured resin appearing not only in the vessels but also in the ground parenchyma tissue (Fig. 4). Water solvent carrier improved the diffusion rate, and as a result, the furfuryl alcohol penetrated more area of the bamboo blocks.

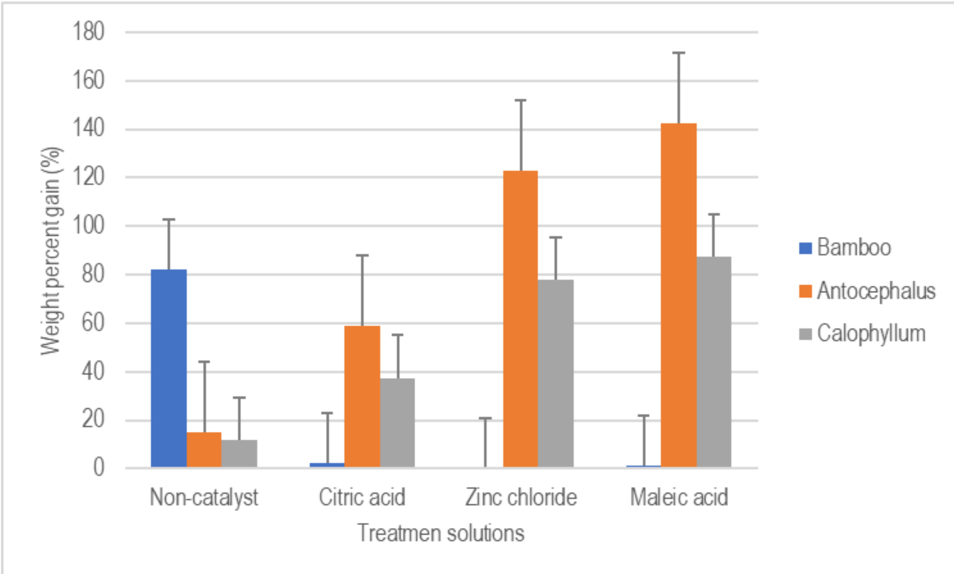


Figure 1. Weight percent gain in bamboo, *Anthocephalus* and *Calophyllum* blocks after furfurylation with catalyst.

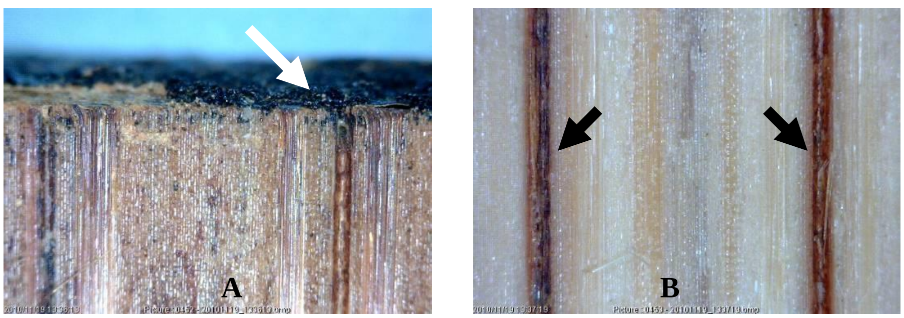


Figure 2. Visual examination of cured bamboo blocks.

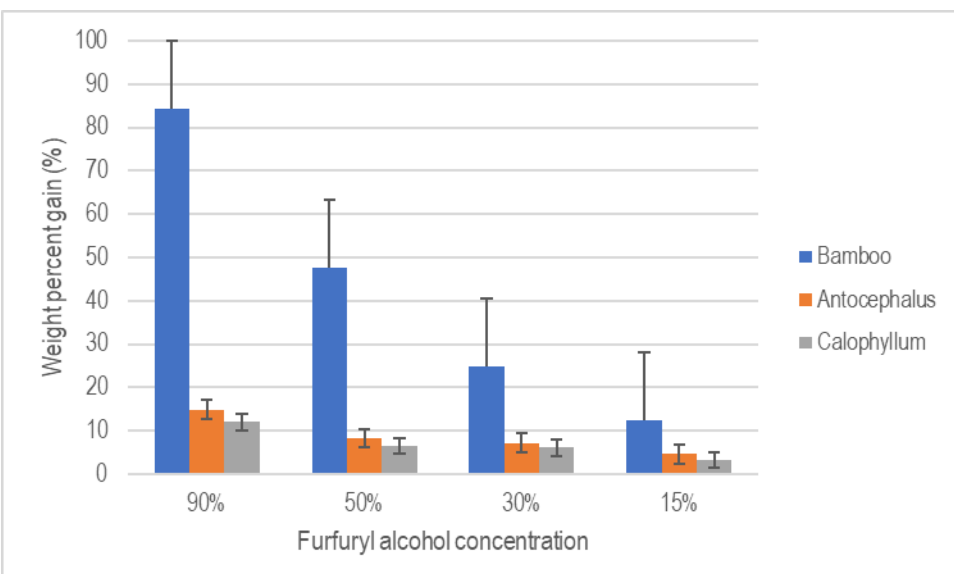
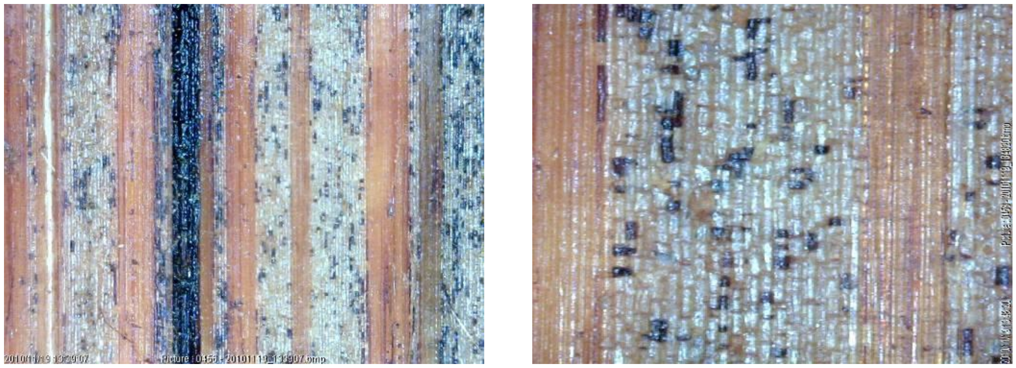


Figure 3. Weight percent gain in blocks with various furfuryl alcohol concentrations.



A B

Figure 4. Visual examination of furfurylated bamboo using water as a carrier solvent.

Conclusions

This study shows that the longer the soaking and vacuuming time, the higher the furfuryl alcohol uptake. The differences in uptake between strip portion (outer, middle and inner) show a clear trend that the outer strips have the highest uptake and the inner strips have the lowest uptake. They were soaking bamboo strips for two days after vacuum treatment achieved optimum uptake of furfuryl alcohol. The uptake improvement after vacuuming and soaking treatments is caused by liquid penetration through vessels during vacuuming followed by solution moving into the surrounding vessels by diffusion.

The addition of a catalyst to furfural alcohol significantly reduced the weight percent gain in bamboo, due to premature polymerization of the alcohol blocking further penetration. Addition of low concentrations (10%) of water to the furfuryl alcohol was optimum in achieving higher chemical uptake in bamboo.

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