Treatment of Caribbean Pine by *In Situ* Polymerization of Styrene and Furfuryl Alcohol

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ABSTRACT: Caribbean pine impregnated by the full cell treatment schedule with styrene, furfuryl alcohol (FFA), and styrene–FFA monomers was cured for 48 h at 100°C. Styrene did not penetrate inside the wood cell wall; instead, it adhered on the cell wall surfaces and fill cell lumens. The volume contraction during the formation of polystyrene causes the volume contraction of the wood sample. The permanent volumetric swelling is attained only for samples treated with FFA, which is caused by cell wall impregnation. The dimensional stability of the treated wood samples is evaluated with the antiswell efficiency coefficient (ASE). The

water repellency is expressed as the water-repellent effectiveness (WRE). Treatment with styrene improves the water repellence, whereas a double treatment increases the dimensional stability. Lixiviation slightly affects the ASE and WRE coefficients. The treatments improve the Shore D hardness in comparison to untreated wood. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 1763–1769, 2004

Key words: solid softwood; impregnation; dimensional stabilization; water repellence; hardness

INTRODUCTION

The difficulties encountered in the use of wood often relate to its dimensional instability to moisture, biodegradability, and flammability. Various approaches have been studied to change these intrinsic characteristics. The treatment of wood to improve its physical and mechanical properties and dimensional stabilization due to moisture content and to impart resistance to termites, decay, and marine organisms has been carried out via chemical modification or chemical impregnation. In chemical modification, compounds that are highly reactive to the hydroxyl groups of the cellulose, hemicellulose, and lignin components of wood include isocyanates,^{1–5} epoxides,^{2,4,6–8} anhydrides,^{2,6,7,9–11} and lactones.^{3,7} Several liquid monomers such as styrene^{2,12,13} and methyl methacrylate^{14,15} are also incorporated into wood samples by means of chemical impregnation. Crosslinking of wood with chemicals^{1,2,3,6,7,16} provides good dimensional stability to the wood–polymer composite.

An important aspect of treatments of solid wood is the selection of a chemical that is compatible with the lignocellulosic substances. Most attempts to stabilize wood with monomers have failed because the monomers did not penetrate the cell walls or did not react with the wood components. For instance, poly(ethylene glycol) (PEG) is highly hygroscopic and does not react with wood components; moreover, it is water soluble and easily leached. Despite the fact that PEG treatment^{1,6,7,12} can improve the dimensional stability of wood during a short exposure to water, the treatment is not resistant to more severe tests.

Furfuryl alcohol (FFA) is a product of the reduction of furfural derived from crop residues.¹⁷ It is a very reactive substance that undergoes acid-catalyzed polymerization,18 forming a black amorphous crosslinked polymer. Catalysis by weak acids or strong diluted acids results in a low concentration solution of short chain oligomers in the FFA monomer that are characterized by a greenish color.^{19,20} This solution is ideal for wood impregnation because of its low viscosity at room temperature and fast polymerization when heat treated at 100°C. Solid wood treated with FFA becomes decay and chemical resistant²¹⁻²³ and its dimensional stability and hardness are increased.²⁴ Stamm²⁵ found that the mechanical resistance to bending decreased and the dimensional stability increased when softwood was treated with FFA. Moreover, FFA resin is a well-known fire resistant material.²⁶⁻²⁸ For all the above reasons, wood treatment with FFA may be an advantageous process.

Polystyrene (PS) has good interfacial adhesion to lignocellulosic fibers.^{29,30} If chemical bonds seal the resin to the lumen walls when the resins are cured inside the wood cell lumen, this should also minimize the water uptake by wood. In wood finishes (e.g., paint and varnish coatings)³¹ a PS film can never be

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entirely moisture proof. The degree of protection provided by different treatments depends on the type of exposure. For example, water-repellent treatments are ineffective against exposure to water vapor but relatively effective against free water for a short exposure time. Thus, for good protection against water vapor and liquid water for a long exposure time, chemical modification of the wood OH sites inside the cell wall is imperative.

Norimoto et al.⁶ classified chemically treated wood according to a double criterion: modifications of the lumens (cellular level) and modification of the cell wall material (molecular level). According to this classification, FFA treatment of softwood can be characterized by a combination of these two criteria. Otherwise, styrene treatment^{2,12,13,32} only promotes lumen filling or cell wall coating, thus being classified as lumen modification.

The objectives of our work were to evaluate the ability of a combination of styrene and FFA to increase the water repellence, dimensional stability, flexural and compression resistance, density, hardness, flame resistance, and resistance to biodegradation.

EXPERIMENTAL

Formulations

Styrene (Sayerlack, Brazil Inc.) was vacuum distilled to eliminate the inhibitor and then 0.5 wt % benzoyl peroxide was added as a catalyst. This monomer solution and the same solution diluted to 50 vol % in dichloromethane (Synth) were used to impregnate wood samples and produce the wood–PS composite.

The FFA (Aldrich) in the study was used as received. Before impregnation, 0.5 wt % *p*-toluene sulfonic acid monohydrate (Riedel) was added as a catalyst. Dichloromethane (DCM) was used as a solvent to control the furfuryl load into the solid wood.

The treatment using the impregnation solution composed of FFA resin and PS resin is referred to as 50/50 FFA/DCM and that with 50 vol % DCM as a solvent is referred to as 50/50 PS/DCM.

A blend of the two formulations above, styrene, and FFA with their respective catalysts (PSFFA) in a volumetric proportion of 50/50 (v/v) were also used to impregnate solid wood.

Wood treatment

Oriented samples ($20 \times 20 \times 20$ mm radial × tangential × longitudinal) of Caribbean pine (*Pinus caribaea hondurensis*) were used. They were cut so that the growth rings were parallel to the tangential face. The samples were oven dried for 24 h at 105°C, cooled in a desiccator over silica gel, and then weighed and measured prior to treatment. The full cell treatment

schedule was used. Wood samples placed and immobilized in a metal tray were put in a pressure cylinder and subjected to a vacuum of 1 Torr for 30 min. The monomer solution was then introduced into the tray until the wood samples were totally immersed. The vacuum was released and the pressure inside the cylinder was raised to about 8 atm (120 psig or 827 kPa) with compressed nitrogen and maintained for 30 min. The pressure was then released and the samples were removed from the tray, weighed, and allowed to air dry before curing. Wood samples impregnated with styrene and FFA monomer solutions were allowed to stand for 24 h at room temperature while wrapped in aluminum foil. Then the samples were polymerized for 24 h at 60°C and cured for 12 h at 100°C. The low-level temperature (60°C) treatment was used to increase the PS molecular chain length with an improvement of the polymer mechanical resistance in addition to minimizing monomer evaporation.

Two methods were used to obtain the double treatment with styrene and FFA. A solution of styrene/ FFA with their respective catalysts was used for the first treatment (PSFFA). For the second treatment (FFA and PS) wood samples were first impregnated by the full cell process with FFA and a catalyst. After FFA impregnation the tray was drained and evacuated to eliminate the alcohol excess, and then the samples were reimpregnated with styrene monomer. The performance of the second impregnation was accompanied by the weight percent gain (WPG) and by the monomer volume absorbed by the samples. As before, the aluminum foil wrapped impregnated samples were allowed to stand for 24 h at room temperature. Then the samples were polymerized for 24 h at 60°C and cured for 12 h at 100°C.

Evaluation of properties of resin-treated wood samples

The ability of the resin formulations to penetrate wood under the applied treatment was determined by treating the Caribbean pine cubes. The resin solution retention (RSR) before air drying, the solid resin retention (SRR) after curing, and the WPG after curing were used as the criteria of treatability. These values were calculated as follows:

$$RSR = (W_1 - W_0)/volume of sample$$

 $SRR = (W_2 - W_0)/volume of sample$

WPG =
$$(W_2 - W_0)/W_0 \times 100$$

where W_1 is the weight of the treated sample after impregnation, W_2 is the weight of the treated sample after curing, and W_0 is the weight of the untreated sample. Some treatments cause permanent volumetric swelling of the samples. These values were calculated as the percentage of the initial volume of the untreated sample.

Rowell and Ellis³³ reported that erroneous results were obtained when determining dimensional stabilization by the water soak method if only one soak/dry cycle was used. Thus, they recommend that at least three such cycles be employed. In this work, treated wood samples were subjected to a series of four watersoak/dry cycling tests.

The properties of treated and untreated wood samples were reported from the averages of 10 experimental results for each test. The dimensions of the treated and untreated samples were monitored with vernier calipers after four cycles of repeated wetting and drying. The dimensional stability of the impregnated wood samples was evaluated as the antiswelling efficiency (ASE) and the measured volume changes (ΔV %). All uptake and polymer retention is reported on an oven-dry wood basis. The degree of dimensional stability generated by the treatment was assessed during four oven-dry/water-soak cycles. Each cycle included oven drying the sample at 105°C until constant weight, measuring its dimensions, then soaking it in fresh water for 4 days and remeasuring it at 12, 24, 48, 72, and 96 h.

The dimensional stability was expressed as the ASE determined from eqs. (1) and (2):

$$S = (V_2 - V_1) / V_1 \times 100 \tag{1}$$

where *S* is the volumetric swelling coefficient, V_1 is the wood volume of the oven-dried sample (24 h, 105°C) before the water soaking test, and V_2 is the wood volume after the test. The sample volume, which is used as a dry base after each cycle for the ASE calculations, was measured after oven drying the samples in the anterior cycle.

$$ASE = (S_2 - S_1) / S_1 \times 100$$
 (2)

where S_1 is the volumetric swelling coefficient for treated wood and S_2 is that for untreated wood.

The water repellency was expressed as the WRE. The WRE values are defined by the water uptake versus the time data obtained by soaking the wood samples in water. The WRE values were calculated using the following formula:

$$WRE = (D_c - D_t)/D_c \times 100$$

where D_c is the water uptake of the control and D_t is the water uptake of the treated sample, calculated as

$$D_c \text{ or } D_t = (w_2 - w_1)/w_1 \times 100$$

TABLE I Treatability of Caribbean Pine with PS, FFA, and PS/ FFA Resins

	$\frac{\text{RSR} \pm \text{SD}}{(\text{kg}/\text{m}^3)}$	$\frac{\text{SRR} \pm \text{SD}}{(\text{kg/m}^3)}$	WPG ± SD (%)	
50/50 PS/DCM PS PSFFA FFA/PS 50/50 FFA/DCM FFA	$560 \pm 12 505 \pm 12 503 \pm 11 543 \pm 13 765 \pm 18 730 \pm 19$	$\begin{array}{c} 122 \pm 9 \\ 377 \pm 10 \\ 167 \pm 16 \\ 177 \pm 16 \\ 162 \pm 19 \\ 352 \pm 47 \end{array}$	$21 \pm 266 \pm 324 \pm 231 \pm 333 \pm 372 \pm 9$	

where w_1 is the initial weight and w_2 is the weight after water immersion. After each water-soaking cycle the samples were oven dried and the weights were measured in order to evaluate the leaching of the chemicals.

The hardness of untreated and treated solid wood was measured by a Shore D hardness tester. The measurements were performed on dried and 65% relative humidity air-conditioned samples after the four water immersion cycles. The Shore D hardness values were determined on the tangential surfaces of the samples.

Scanning electron microscopy (SEM) was used to examine the interaction of the polymer with the wood cell walls. Interior cross sections were examined. These were sputter coated with gold before analysis. All SEM analyses were carried out using a Zeiss 980 (DSM).

RESULTS AND DISCUSSION

Wood treatability

The treatability of wood with PS, FFA, PSFFA, and FFA/PS resins was demonstrated by the RSR after impregnation, the SRR after curing, and the WPG after curing for wood blocks using the full cell process for impregnation and the same curing scheme for all samples. The RSR, SRR, and WPG data are listed in Table I for wood treatments with PS, FFA, PSFFA, and FFA/PS resins.

In addition to the wood structure, there are many factors that affect the treatability of wood. The molecular size or molecular weight, the viscosity of the resin solution, the temperature scheme for resin polymerization, and the polarity of impregnated molecules play important roles in wood treatment.

The treatability data in Table I show that FFA and PS resins are readily impregnated into Caribbean pine. WPG and RSR values as high as 73% and 765 kg/m³, respectively, were achieved. The RSR values were greater for resins with FFA, being more pronounced for resins made only with FFA. This result shows that the affinity of the solid wood with FFA is greater than with styrene. The styrene monomer has an aromatic

TABLE II Average, 10 Replicates Volumetric Swelling (% Initial Volume) after Treatment in Caribbean Pine

Treatment	Permanent swelling \pm SD (%)		
50/50 PS/DCM PS PSFFA FFA/PS 50/50 FFA/DCM FFA	$\begin{array}{c} -1.3 \pm 0.6 \\ -1.0 \pm 0.4 \\ 13.5 \pm 0.6 \\ 10.7 \pm 1.0 \\ 9.4 \pm 2.2 \\ 9.8 \pm 0.9 \end{array}$		

hydrocarbon structure that is responsible for its nonpolar nature. By contrast, FFA has a very polar structure that is prone to hydrogen bonding with the OH of the wood macromolecules.

A more pronounced loss of weight after curing was observed for resins dissolved in DCM because the solvent evaporates and does not react with the wood or with the resins. However, the resins with FFA show a high level of weight loss for two reasons. First, FFA produces water as a condensation reaction by-product during curing. This water evaporates. Second, a loss of weight must occur due to monomer evaporation.

Swelling after treatment

Table II gives the permanent volumetric swelling values after curing. Each value is an average of 10 replicates.

The negative value for the volumetric swelling means that volumetric contraction occurred after curing. Styrene did not penetrate inside the wood cell wall; it just adhered on the cell wall surfaces. The volume contraction during the *in situ* formation of PS causes the volume contraction of the wood sample.

Permanent volumetric swelling was attained only for samples treated with FFA. This is caused by the penetration of the FFA into the wood cell wall because there is compatibility between the polar wood macromolecules and the polar FFA molecules.

Dimensional stability

It is noteworthy that untreated wood and PS-treated wood show a high level of end splitting after the fourth cycle of water immersion. The percent number of cracked samples in the 10 replicates can be found in Table III.

The samples treated with pure PS resin suffered cracking after the fourth cycle, which means that the ASE and WRE coefficients are impossible to estimate reliably. The most efficient treatments against end splitting were with FFA resins.

Despite the fact that the PS resin adheres on the internal wood surfaces and causes wood volume contraction after the resin has cured, the PS treatment does not prevent wood swelling. As wetting progresses during the water immersion test, the wood cell wall begins to absorb water and attempts to swell. However, the wood cell wall surface is set at a permanently contracted condition by the cured PS resin and this prevents normal swelling of the cell wall. This causes severe internal tension stresses beyond the rupture limit, thus resulting in internal cracks.

The percentage of end splitting for the double treatment FFA/PS is greater than for the PSFFA. When FFA and PS are impregnated together, the adhesion of the PS resin to the cell wall decreased compared to the individual impregnation treatment.

The FFA treatments cause permanent swelling by impregnation of the wood cell wall and preventing the access of water molecules for further swelling.

ASE and WRE measurements

The ASE and WRE measurements evaluate the dimensional stability of the treated wood. The ASE coefficients can be seen in Figure 1 for all treatments measured after each cycle of the immersion test. The results shown in Figure 1 are related to samples that do not suffer end splitting after each cycle. The negative values for the ASE coefficient mean that the sample swelled more than the untreated wood.

After the first immersion cycle the best ASE coefficient value (82%) was attained by the FFA treatment. Indeed, the treatments with FFA in the formulation of the impregnation solution presented the best results. However, the ASE values decreased after the second water immersion cycle for FFA and 50/50 FFA/DCM treatments. This behavior is attributed to the lixiviation of the chemicals, which were not 100% cured inside the wood cell wall. On the other hand, the worst ASE value (-16%) was for the 50/50 PS/DCM treatment.

Both double treatments did not show substantial variation of the ASE values along the water immersion cycles. PS coats the wood cell wall surfaces, thus creating a barrier against water; moreover, FFA mole-

 TABLE III

 Percentage of Samples That Suffer Cracking in 10

 Replicates after Each Cycle of Water Immersion Test

Treatment	After cycle				
	1	2	3	4	
Untreated	0	0	0	30%	
50/50 PS/DCM	0	0	50%	90%	
PS	0	20%	50%	100%	
PSFFA	0	10%	40%	50%	
FFA/PS	0	10%	70%	70%	
50/50 FFA/DCM	0	0	0	10%	
FFA	0	0	0	10%	



Figure 1 The variation of the coefficient of the antiswell efficiency (ASE) with the water immersion cycles of the treated wood samples.

cules impregnate the wood cell wall and impede the water penetration by a bulk effect. Therefore, at the end of the fourth water immersion cycle the FFA/PS treatment presented almost the same ASE coefficient as the FFA treatment.

Solid wood behaves like a chromatographic material when impregnated by the PSFFA solution. Most of the FFA is absorbed by the wood cell wall whereas the styrene remains at the lumen.

After several cycles of the water immersion test, the best efficiencies for dimensional stabilization were attained for treatments with FFA.

Wood samples treated with PS suffer increasing internal cracking with water immersion time, thus increasingly exposing new wood cell wall surfaces to water molecules. These water molecules swell wooden substances; moreover, internal cracking causes volume expansion. Both things result in a loss of dimensional stabilization properties.

One important observation is that permanent swelling of the wood sample is required for good dimensional stabilization. However, the best ASE value was not attained for the greatest permanent volume swelling. For instance, the PSFFA double treatment promoted the greatest permanent swelling (13.5%) and the ASE value (30.4%) was less than for FFA (82.2%), 50/50 FFA/DCM (70.0%), and PS/FFA (46.7%) treatments.

The WRE coefficient value can be seen in Figure 2 for all treatments measured after each cycle of the immersion test, even for the samples that suffer end splitting.

The best result for the WRE coefficient value (78% after the first cycle) was attained for treatment with pure PS resin, even after the fourth water immersion

cycle. Despite the high level of end splitting for PStreated samples, the PS resin was efficient in repelling liquid water. In contrast, the worst WRE value (34%) was obtained for the 50/50 FFA/DCM treatment.

The FFA treatment presented high water repellence with WRE values that were better than for the PSFFA double treatment. An FFA treatment with a low WPG means that the resin is in the cell walls but the cell lumen is empty, leading to low WRE values. However, PS treatment with a high WPG fills the cell lumen without cell wall impregnation and with high WRE values. The filling of the cell lumen with hydrophobic polymers that have good adherence to the cell wall is important for water repellence.

The wood WPG for the double treatments is assigned to both polymers that are formed. Poly(FFA) is preferentially formed inside and onto the cell walls and the PS inside the cell lumen. The WPG values for PSFFA and FFA/PS are 24 and 31, respectively. Thus, the amount of polymer formed in the cell lumen is less than that formed during the 50/50 PS/DCM treatment. Moreover, the monomers impair the polymerization of the each other. These facts explain why the PSFFA and FFA/PS presented WRE values that were less than those of the PS and FFA treatments.

Lixiviation

Figure 3 shows the weight percent loss caused by leaching of the water-soluble extractives and chemicals for untreated and treated wood samples after the water immersion cycles.

Leaching of the chemicals is greatest for the FFA treatment, followed by untreated and 50/50 FFA/DCM treatment. The lixiviation of the samples treated



Figure 2 The variation of the coefficient of water repellency efficiency (WRE) with the water immersion cycles of the treated wood samples.



Figure 3 Lixiviation of the treated and untreated wood after each water immersion cycle.

only with FFA or FFA diluted in DCM explains the reduction of the ASE values with increasing water immersion cycles.

PS filled the cell lumen and/or coated the cell wall, as can be seen below in the SEM analysis, thus avoiding leaching of extractives. Furthermore, the treatment attained almost completely cured PS that is water insoluble.

Cured poly(FFA) is also insoluble in water; however, the heat treatment probably did not convert all the monomer inside the cell wall into a crosslinked structure. In addition, part of the furan ring may have opened and formed ketone and/or levulinic acid.³⁴ In fact, FFA monomers, oligomers, and fission products are water soluble.

Shore D hardness

Treated solid wood samples show higher Shore D hardness than that shown by untreated wood (see Fig.



Figure 5 SEM micrography of the cross section of (A) PSand (B) FFA-treated wood.

4). The highest hardness value (76 \pm 5) was attained for the pure PS treatment. The PSFFA and pure FFA treatments show almost the same value as the PS treatment. The high hardness value for PSFFA-treated wood is noteworthy, despite the low WPG level attained by the treated samples.

SEM analysis

Figure 5 shows the micrography of the cross sections of PS- and FFA-treated wood. Observe in Figure 5(A) that the polymerized styrene fills the cell lumens. This fact justifies the high WRE and hardness values attained by the treatment. Figure 5(B) shows that the FFA treatment did not completely fill all the cell lumen, despite the high WPG attained. Thus, in the FFA treatment the resin should have penetrated inside the cell wall, confirming the permanent volumetric swelling of the wood block. Moreover, the FFA treatment causes high dimensional stability.

Figure 6 shows the SEM micrography of the cross section of PSFFA- and FFA/PS-treated wood. The PS-FFA-treated wood [Fig. 6(A)] presents a denser structure than the FFA/PS-treated wood [Fig. 6(B)]. Thus, the WRE values for a PSFFA treatment are higher than for the FFA/PS treatment.

Figures 5 and 6 show no noticeable gaps between the polymer and the cell wall. We then deduced that PS adhered to the cell wall; moreover, FFA does not



Figure 4 The Shore D hardness values of treated and untreated wood after the fourth cycle of water immersion.



Figure 6 SEM micrography of the cross section of (A) PSFFA- and (B) FFA/PS-treated wood.

impair the PS adhesion during both double treatments of FFA with PS and PSFFA.

CONCLUSIONS

The PS and FFA treatments provide high WPGs for the Caribbean pine. The impregnation of both resins, together or concomitant, promotes a high level of resin retention. However, the *in situ* polymerization is impaired, resulting in a low level for the WPG.

Treatments with FFA promote permanent volumetric swelling and the highest dimensional stabilization, despite lixiviation after several hours of water immersion. Treatment using only styrene resin results in volume contraction and a high level of water repellence; however, the treatment promotes end splitting and low values for the ASE.

The treatments using both resins, styrene and FFA, result in intermediate values for the dimensional stability, water repellence, and hardness.

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