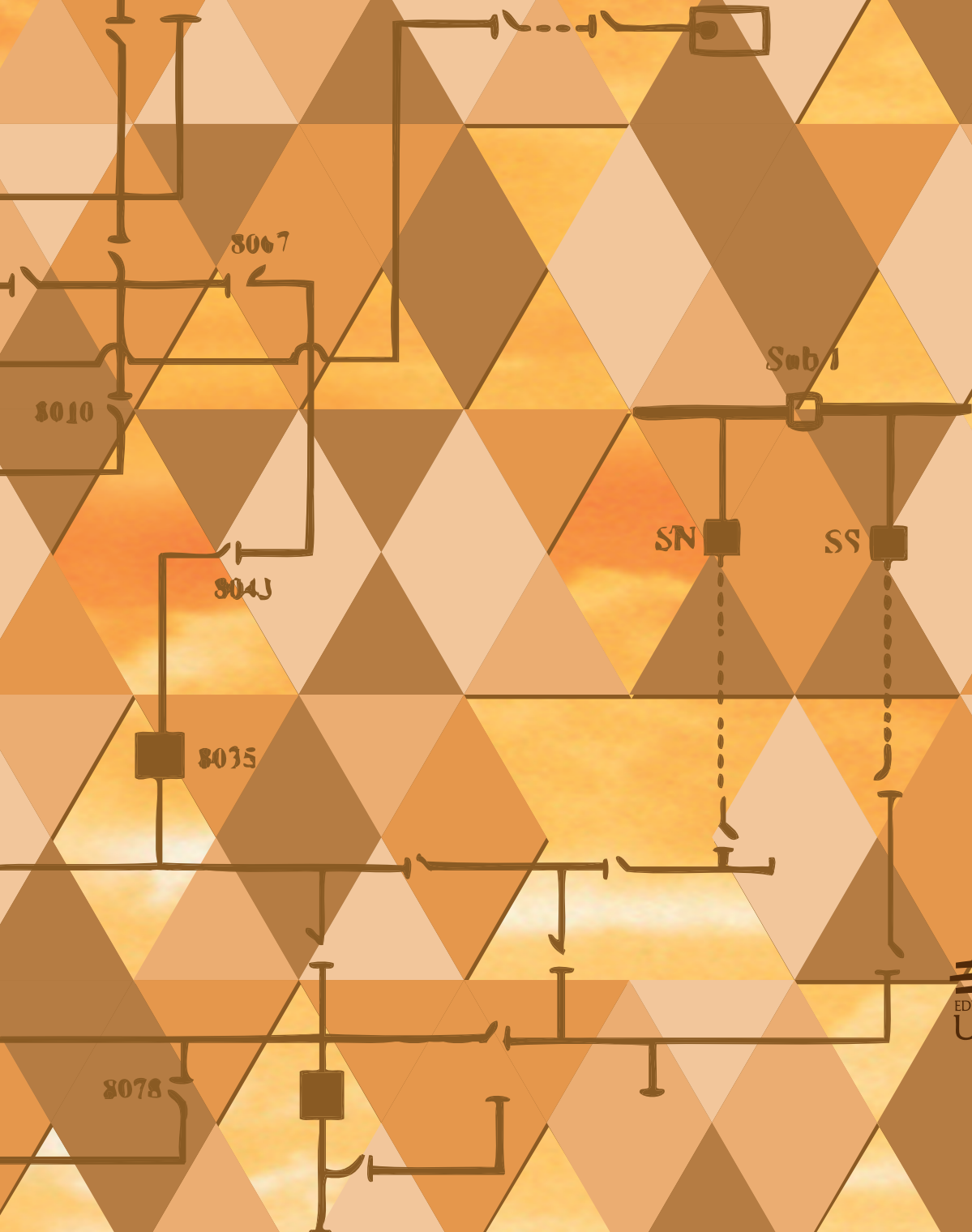


Ingeniería

Revista de la Universidad de Costa Rica
FEBRERO/AGOSTO 2014 - VOLUMEN 24 Número (1)



DIMENSIONAL STABILITY OF WOOD OF TEAK AND MELINA TREATED WITH ACETIC ANHYDRIDE

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Abstract

The dimensional stability of chemically modified solid samples of the tropical hardwood species Teak (*Tectona grandis*) and Melina (*Gmelina arborea*) was studied. Samples of both species were modified using acetic anhydride as reagent, and reaction time was changed to obtain different values of weight percent gain (WPG). Dimensional stability was determined using five cycles of water impregnation and drying of the samples in an oven. Volume changes were measured, and the volumetric swelling coefficient (S%) and anti-swelling-efficiency (ASE%) were calculated. It was found that S% decreases as reaction time increases, whereas the ASE% rises with increasing reaction time for both species, thus improving the dimensional stability of both hardwoods.

Keywords: Acetic anhydride, Acetylation, Dimensional stability, Tropical hardwood.

Resumen

Se estudió la estabilidad dimensional de muestras sólidas modificadas químicamente de las especies maderables tropicales Teca (*Tectona grandis*) y Melina (*Gmelina arborea*). Venticuatro. Muestras de ambas especies fueron modificadas utilizando anhídrido acético como reactivo y el tiempo de reacción fue cambiado con la finalidad de obtener distintos valores de ganancia en peso (WPG). La estabilidad dimensional fue determinada por medio de cinco ciclos de impregnación con agua y secado de las muestras en un horno. Los cambios en el volumen fueron medidos para calcular el coeficiente volumétrico de hinchazón (S%) y la eficiencia de anti-encogimiento (ASE%). Se encontró que el S% disminuye conforme incrementa el tiempo de reacción y que el ASE% se incrementa con el tiempo de reacción para ambas especies, con lo cual, se mejora la estabilidad dimensional de ambas maderas tropicales.

Palabras clave: Anhídrido acético, Acetilación, Estabilidad dimensional, Madera tropical.

Recibido: 14 octubre de 2013 • **Aprobado:** 16 de enero de 2014

1. INTRODUCTION

The chemical modification of wood can be considered as a chemical process in which a reagent and a reactive group of the wood polymeric cell wall interact in order to form a new bond between the two compounds (Rowell, 2006). Most of the reactions studied for this purpose involve the hydroxyl group of the cell wall (Hill, 2006). Indeed, different

types of reagents have been used to achieve this transformation, including anhydrides (acetic, butyric, phthalic), carboxylic acids, acetaldehyde, formaldehyde and epoxides; however, only acetylation (using acetic anhydride) have surpassed the research stage (Rowell, 2006). Acetylation induces ester bonds between acetic anhydride (AA) and hydroxyl groups, creating stable acetyl groups which are resistant to water (Rowell *et al.*, 1982).

On a small scale, the dimensional stability of wood is determined by measuring the external dimensions of small samples (Hill, 2006). One method, proposed by Rowell and Ellis (1978), is based on the dimensional changes caused by ambient conditions, where humidity takes the main role. In this method sample dimensions are first measured after oven drying and then are impregnated with water using a vacuum pump and are submerged for days. Their dimensions are measured again, and then the cycle is repeated for several times.

Using this measuring method several studies had been conducted in order to determine the dimensional stability of modified species, i.e., Tillman *et al.* (1987) modified commercial Pine and Birch with AA and they found that ASE% is up to 40 % for WPG of 7-10 %, thus concluding that acetylation decreases the rate and the level of swelling due to water saturation.

Nevertheless, Ramsden *et al.* (1997) studied the effect of acetylation on Pine (*Pinus silvester*) samples using AA with xylene. It was determined that the volume increase due to the water saturation of acetylated samples was minimal, concluding that the reduction of active hydrogen to form bonds with water causes an increase in the dimensional stability of acetylated wood. Furthermore, anti-swelling efficiencies due to acetylation of up to 60% have been achieved (Tarkow *et al.*, 1950; Kumar *et al.*, 1982; Koppers, 1961).

Therefore, it has been demonstrated that the chemical modification of wood with anhydrides of straight-chain carboxylic acids improves the dimensional stability of softwoods, but to the best of our knowledge, no results for hardwoods have been published in the open literature, which are native of tropical weather. Thus, the main purpose of this work is to study the dimensional stability of treated wood of the tropical hardwood species Teak (*Tectona grandis*) and Melina (*Gmelina arborea*) using acetic anhydride to calculate the volumetric swelling coefficient (S%) and anti-swelling efficiency (ASE%), which are variables related to dimensional stability.

2. MATERIALS AND METHODS

Samples were prepared of *Tectona grandis* wood obtained from the Atlantic region and

Gmelina arborea wood obtained from the San Carlos region of Costa Rica, both 8 years old, from one tree and no differentiation between sapwood and hardwood was made, taking into account that industrial processes do not make this differentiation either.

Twenty-four samples were prepared with dimensions 1,5 cm x 1,5 cm x 1,0 cm for each species, which were treated with 250 mL of a mixture of toluene-ethanol (2:1 v/v) for 8 hours and 250 mL of distilled water for 8 hours. Then, the wood samples were oven dried at 103 °C for 16 hours and cooled to room temperature in a desiccator containing silica.

An excess of 30% of AA and potassium carbonate (0,05 g K₂CO₃/g dry wood) was used according to the dried weight of every sample. Dimethylformamide (DMF) was used as solvent and dried with molecular sieves of 4 Å to secure an anhydrous environment. The samples were then added and subjected to vacuum/atmospheric pressure cycles to pre-impregnate the wood with the reagent solution.

The reaction conditions were 1,6 mL of AA for each gram of dry wood, and the temperature was fixed at 70 °C. The values of the reaction time were selected for one, three and six hours with the purpose of changing WPG. Eight samples for each reaction time were used for each species. The reactions were performed in a round-bottomed flask equipped with a condenser and a drying tube with calcium chloride. Once the reaction was finished, samples were extracted using a Soxhlet equipment with a benzene/ethanol/acetone (4:1:1 v/v) solution for 8 hours to remove unreacted compounds, DMF, and other by-products. Then, the blocks were oven dried at 103 °C for 16 hours and cooled to room temperature, and the resulting weight percent gain (WPG) was calculated as:

$$WPG = (M_f - M_s) / M_s \cdot 100 \quad (1)$$

Where:

M_s = oven dried weight of the untreated block.

M_f = oven dried weight of the acetylated wood.

Acetic anhydride, DMF, toluene, and benzene were purchased from J.T. Baker and

Table 1. Initial and final volumes of eight samples of Teak.

Time (h)	Cycle	Initial volume (cm ³)	SD	Final volume (cm ³)	SD
Control	1	2,515	0,050	2,691	0,024
	2	2,495	0,047	2,684	0,025
	3	2,482	0,051	2,681	0,023
	4	2,491	0,053	2,710	0,028
	5	2,493	0,044	2,668	0,024
1	1	2,376	0,138	2,522	0,021
	2	2,353	0,134	2,525	0,019
	3	2,361	0,141	2,543	0,023
	4	2,368	,0,136	2,571	0,026
	5	2,384	0,133	2,540	0,037
2	1	2,445	0,126	2,578	0,023
	2	2,410	0,130	2,588	0,023
	3	2,409	0,128	2,599	0,023
	4	2,421	0,135	2,597	0,022
	5	2,427	0,136	2,580	0,021
6	1	2,512	0,127	2,629	0,008
	2	2,483	0,116	2,648	0,013
	3	2,475	0,114	2,662	0,017
	4	2,488	0,109	2,660	0,012
	5	2,501	0,125	2,640	0,010

ethanol was purchased from Gamma Reactives in San José, Costa Rica.

To study the dimensional stability of acetylated samples, control samples were also used. A similar procedure is described in Hill and Jones (1996). All samples were oven-dried for a minimal time of 12 hours, and then the initial dimensions were measured using a digital caliper to the closest millimeter. Later, the samples were vacuum-impregnated with distilled water for water-soak tests, and then were soaked for three days before determining their water-saturated volume. Following measurement, the blocks were dried in an oven at 103 °C for another 12 hours to ensure

that the samples were completely dried. Once fully dried, the samples were measured again and re-weighed. This procedure was repeated for a total of five cycles of oven-dry and water-soak tests.

The volumetric swelling coefficient (S%) was calculated using the following formula (Stamm 1964):

$$S\% = (V_w - V_d) / V_d \cdot 100 \quad (2)$$

Where:

V_w = Volume of water saturated wood

V_d = Volume of dried wood

Table 2. Initial and final volumes of eight samples of Melina.

Time (h)	Cycle	Initial volume (cm ³)	SD	Final volume (cm ³)	SD
Control	1	2,648	0,087	2,947	0,039
	2	2,668	0,086	2,972	0,032
	3	2,694	0,116	2,991	0,040
	4	2,714	0,132	2,958	0,031
	5	2,702	0,119	2,931	0,033
1	1	2,678	0,149	2,901	0,016
	2	2,688	0,161	2,923	0,928
	3	2,640	0,118	2,926	1,438
	4	2,691	0,174	2,909	0,928
	5	2,644	0,148	2,897	0,020
2	1	2,637	0,088	2,841	0,025
	2	2,658	0,100	2,852	0,865
	3	2,660	0,118	2,872	1,438
	4	2,667	0,100	2,870	1,482
	5	2,668	0,094	2,842	0,022
6	1	2,646	0,120	2,789	0,023
	2	2,637	0,123	2,799	0,886
	3	2,635	0,127	2,808	2,223
	4	2,670	0,131	2,823	2,424
	5	2,650	0,115	2,786	0,025

The anti-swelling efficiency (ASE%) was calculated as:

$$ASE\% = (S_{c,mean} - S_{a,mean}) / S_{c,mean} \cdot 100 \quad (3)$$

Where:

$S_{c,mean}$ = Mean volumetric swelling coefficient of control samples.

$S_{a,mean}$ = Mean volumetric swelling coefficient of acetylated samples.

3. RESULTS AND DISCUSSION

The initial (oven-dry) and final (water-soak) volumes for each cycle are presented for both species (Tables 1 and 2), and the mean values are depicted in Figures 1 and 2. It can be observed that the initial volume for each oven dry-water soak cycle is similar to the preceding one for a particular reaction time, which may lead to infer that water is not gained after the cycle is completed and that the treatment is not being removed.

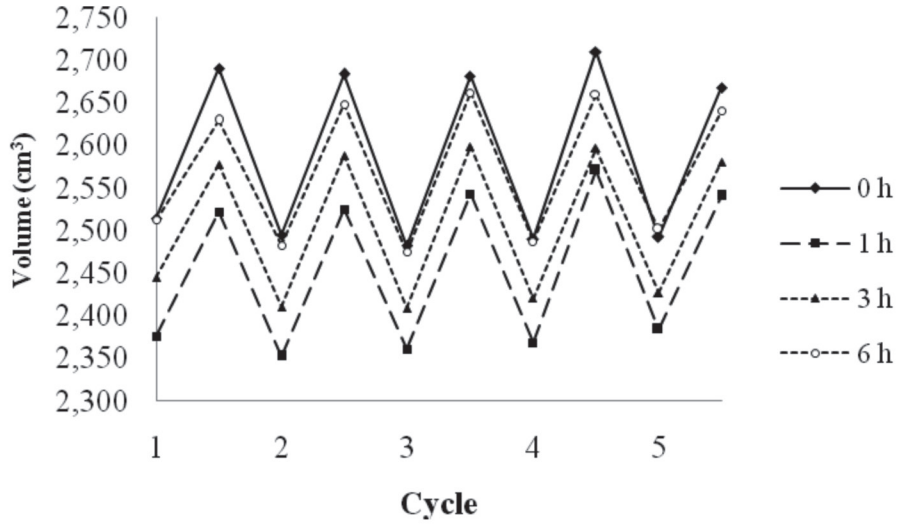


Figure 1. Mean initial and final volumes in function of oven dry-water soak cycles for three reaction times and control samples of Teak.

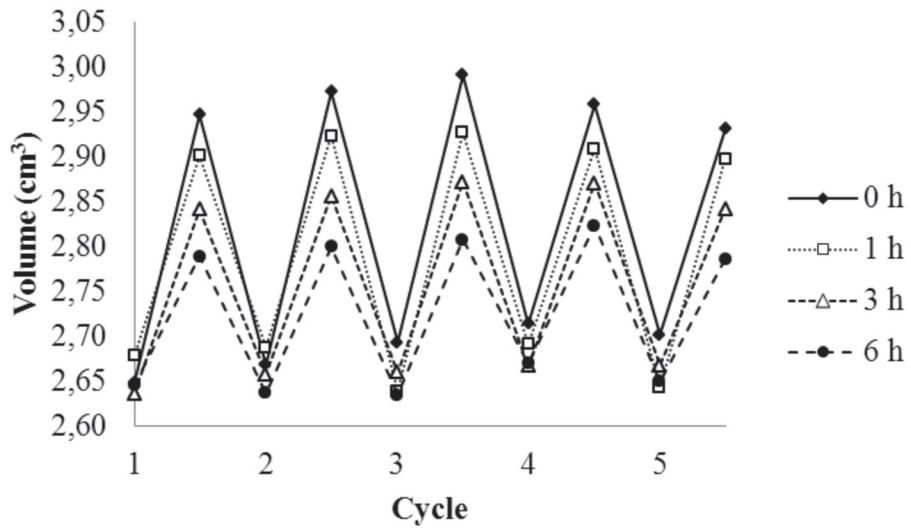


Figure 2. Mean initial and final volumes in function of oven dry-water soak cycles for three reaction times and control samples of Melina.

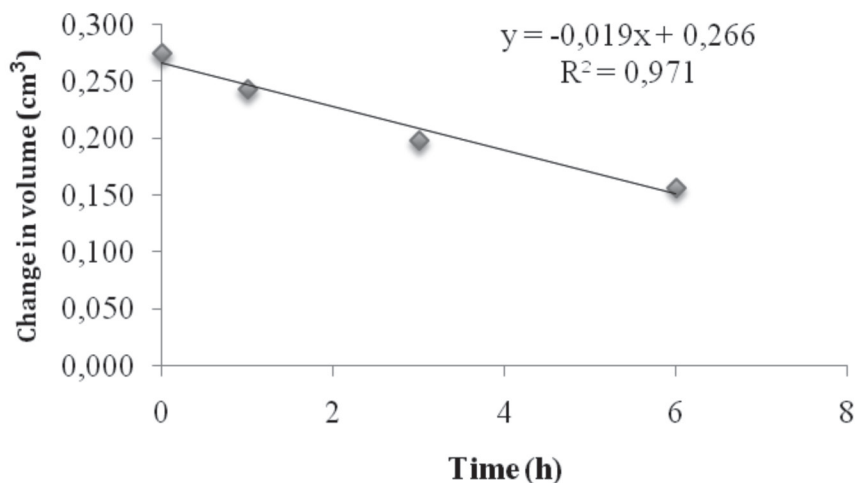


Figure 3. Change in volume for Melina with increasing reaction time.

Table 3. Results of the ANOVA analysis for TEAK.

Source of variability	Degrees of freedom	Sum of squares	Mean square	F	p-value
Time	3	43,420	14,473	5,067	0,0022
Error	156	445,577	2,856		
Total	159	488,997			

Furthermore, we obtained for Teak (Figure 1) that both initial and final volumes remain almost unchanged during the oven dry-water soak cycles; where as for Melina, the average volume change between initial and final volumes decreases for increasing reaction times (Figure 3).

Additionally, the volumetric swelling coefficient (S%) for both species as a function of time of reaction (Figure 4) is observed to decrease at increasing reaction times. This inference is also supported by the data provided in Tables 3 and 4, where the ANOVA analysis for both species concludes that reaction time is a significant factor that affects S% at a 95 % level of confidence, since

the p-value is smaller than 0,05. Furthermore, a higher amount of hydroxyl groups is substituted for acetyl groups according to the reaction time, hence, this substitution is directly related to the smaller quantity of water that treated samples can absorb; thus, the dimensional gain due to water saturation is diminished with increasing reaction times.

It should be stressed that S% changes randomly within oven dry-water soak cycles, which is very common in treatments with a lower number of these cycles and provides evidence that a loss of acetylation has not occurred in contact with water. Nevertheless, further research should focus on longer experiments

Table 4. Results of the ANOVA analysis for MELINA.

Source of variability	Degrees of freedom	Sum of squares	Mean square	F	p-value
Time	3	455,382	151,794	36,845	0,0000
Error	156	642,688	4,120		
Total	159	1098,070			

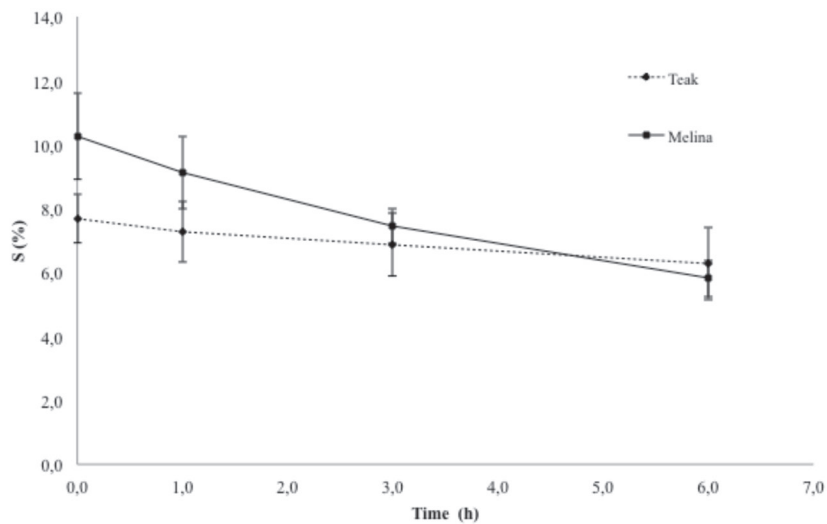
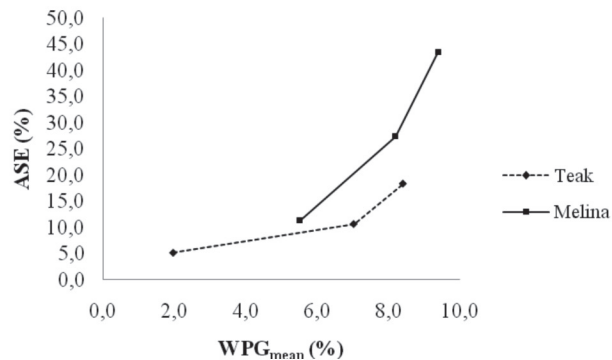
**Figure 4.** Mean volumetric swelling coefficient (S%) as a function of reaction time for Teak and Melina.**Figure 5.** Mean anti-swelling efficiency (ASE%) as a function of WPG for Teak and Melina.

Table 5. S% and ASE% obtained for different species.

Species	WPG(%)	S%	ASE%	Reference
Teak (<i>Tectona grandis</i>)	8,4	6,3	18,3	This work
Melina (<i>Gmelina arborea</i>)	9,4	5,8	43,4	This work
Commercial pine	19,8		69,4	Tillman, <i>et al.</i> , 1987
Corsican pine	27,0 approx	4 approx	75 approx	Hill & Jones, 1996
Pine	22,5		70,3	Rowell, <i>et al.</i> , 2005
Maple	12,89	6,71	59,06	Chang & Chang, 2002

with a higher number of cycles for each species in order to confirm the results obtained, as proposed by Hill and Jones (1996).

On the other hand, the anti-swelling efficiency (ASE%) has been calculated using the mean S% of treated and control samples (Figure 5) as described in Equation (3). According to Hill & Jones (1996), ASE% is an indicator of dimensional stability for the treated samples, which can be used to claim that a dimensional stability of 20 % and 43 % has been reached for Teak and Melina, respectively, treated for six hours.

Moreover, for other softwood species that have been treated with AA, a dimensional stability of 90 % has been reached with WPG as high as 90 %, which clearly shows that for these tropical hardwoods a lower WPG might be sufficient in order to achieve a behavior similar to that of softwoods. Table 5 also presents some values of S% and ASE% according to WPG for previous studies of softwood species and clearly supports that for these tropical hardwood species, better dimensional stability can be achieved with lower WPG than that achieved in softwood species. Although a dimensional stability of 100 % cannot be achieved (Hill & Jones 1996), longer reaction times of acetylation might be necessary in order to increase WPG and ASE% since an asymptotic trend at higher WPG values has not been observed in Figure 5.

4. CONCLUSIONS

This work demonstrates that an improvement in the dimensional stability of the hardwoods studied is achieved with the acetylation treatment using acetic anhydride. Also, according to S%, dimensional growth due to water saturation is lower in acetylated samples relative to control samples from both species, where the average S% at six hours of reaction was 6,3 % for Teak and 5,8 % in Melina. Furthermore, ASE% shows values of up to 18,3 % for Teak and 43% for Melina, which represents an enhancement in the dimensional stability of treated wood for both species. Nevertheless, our experiments suggest that the effect of the treatment is not getting lost when the samples enter in contact with water; however, longer contact times with water are recommended to confirm this statement.

ACKNOWLEDGMENTS

This research was funded by Vicerrectoría de Investigación de la Universidad de Costa Rica from the research project number 731-B2-242. The authors thank Pedro Rojas from Laboratorio de Productos Forestales for his help in the initial preparation of the samples.

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