



Maderas. Ciencia y Tecnología

ISSN: 0717-3644

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Universidad del Bío Bío

Chile

Giridhar, B.N.; Pandey, K.K.; Prasad, B.E.; Bisht, S.S.; Vagdevi, H.M.  
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Maderas. Ciencia y Tecnología, vol. 19, núm. 1, 2017, pp. 15-20

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## DIMENSIONAL STABILIZATION OF WOOD BY CHEMICAL MODIFICATION USING ISOPROPENYL ACETATE

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### ABSTRACT

Chemical modification of wood with isopropenyl acetate (IPA) using iodine ( $I_2$ ) as catalyst has been carried out. Rubber wood (*Hevea brasiliensis*) specimens were reacted with IPA using iodine ( $I_2$ ) catalyst at 95°C up to 10 h under solvent free conditions. The effect of catalyst concentration and reaction time was studied. The extent of acetylation was measured by determining weight percent gain and the modified wood was characterized by FTIR-ATR and  $^{13}C$  NMR spectroscopy. It was found that IPA in the presence of iodine is an excellent acylating reagent for wood. Modified wood exhibited high dimensional stability.

**Keywords:** Chemical modification, dimensional stability, iodine, isopropenyl acetate, rubberwood.

### INTRODUCTION

Wood is hygroscopic, dimensionally unstable especially in high humidity environment and prone to biological decay due to fungus and other microorganisms (Rowell 1983, 2013). All the major cell wall constituents of wood (lignin, cellulose and hemi-celluloses) contain an abundance of free hydroxyl groups. These free hydroxyl groups absorb and release water upon changes in the climatic conditions resulting in dimensional movements of wood. The dimensional stability and biological resistance of wood can be improved considerably by chemical modification by converting hydrophilic -OH groups of cell wall components into larger more hydrophobic groups by forming covalent bonds (Rowell 1983, 2013, Matsuda 1996, Hill 2006). Modification with thermosetting resins improves compression strength and performance against marine borers (Lopes *et al.* 2014, 2015). Treatment with tall oils also reduced water absorption (Can and Sivrikaya 2016). Modified wood has outstanding dimensional stability, improved durability towards insects and micro-organisms.

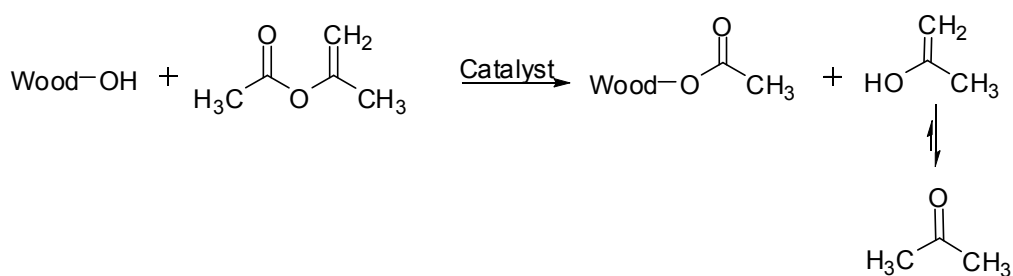
Chemical modification of grounded wood has been carried out by transesterification with vinyl esters (Jebrane *et al.* 2009). Giridhar and Pandey (2016) reported chemical modification of wood by transesterification using IPA in presence of  $AlCl_3$  as catalyst and examined dimensional stability and UV resistance of modified wood. In this work, chemical modification of wood with isopropenyl acetate (IPA) in presence of iodine ( $I_2$ ) catalyst was carried out. The reaction of wood with IPA forms acetone as byproduct (Figure 1) which can be easily removed from modified wood.

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Received: 30.05.2016 Accepted: 02.10.2016



**Figure 1.** Scheme of reaction between wood and isopropenyl acetate (IPA).

## MATERIALS AND METHODS

The specimens of rubberwood (*Hevea brasiliensis*) measuring 20 x 20 x 10 mm<sup>3</sup> were prepared from defect free wood. Specimens were extracted with a mixture of ethanol:acetone:toluene (1:1:4) for 6 h in a Soxhlet apparatus and then oven dried at 100-105°C and their weights were determined.

Isopropenyl acetate (IPA) (99% AR Grade) was purchased from M/s Sigma Aldrich, Bengaluru, India. Iodine (I<sub>2</sub>) (AR Grade) was purchased from M/s SD Fine Chemicals, Bengaluru, India. Oven-dried specimens of rubberwood were reacted with IPA in a reaction vessel containing preheated IPA and a desired amount of I<sub>2</sub>. The concentration of I<sub>2</sub> varied from 0,02 mol L<sup>-1</sup> to 0,035 mol L<sup>-1</sup>. The reaction was carried out at 95°C for different durations up to 10 h. Modified specimens were then soaked in cold acetone to stop the reaction and subsequently extracted with acetone:toluene (1:1) to remove un-reacted reagents and oven dried to determine weight percent gain (WPG). WPG of specimens was calculated using equation;

$$\text{WPG} = \left[ (W_m - W_o) / W_o \right] \times 100 \quad (1)$$

where  $W_o$  and  $W_m$  are oven dried weight of unmodified and chemically modified wood samples, respectively.

The volumetric swelling coefficient (S) and anti-swelling efficiency (ASE) were determined based on the water-soaking method (Rowell and Ellis 1978).

$$S (\%) = 100(V_2 - V_1) / V_1 \quad (2)$$

where  $V_2$  is the volume of saturated sample and  $V_1$  is volume of oven dried sample.

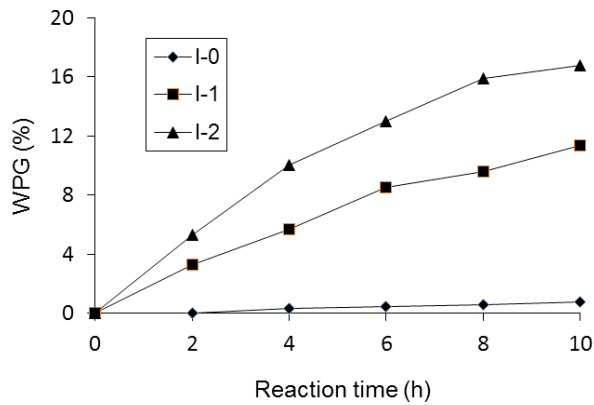
$$\text{ASE} (\%) = 100(S_u - S_m) / S_u \quad (3)$$

where  $S_u$  and  $S_m$  are volumetric swelling coefficients of unmodified and modified samples, respectively.

The ATR-FTIR spectra were measured directly on the wood surfaces (Bruker Germany, Tensor-27 model FTIR Spectrometer; spectral resolution 4 cm<sup>-1</sup>; 64 scans). Solid state NMR spectra were obtained by a JEOL ESX 400 MHz, CP/MAS <sup>13</sup>C NMR spectrometer at the NMR Research Center, Indian Institute of Science, Bengaluru.

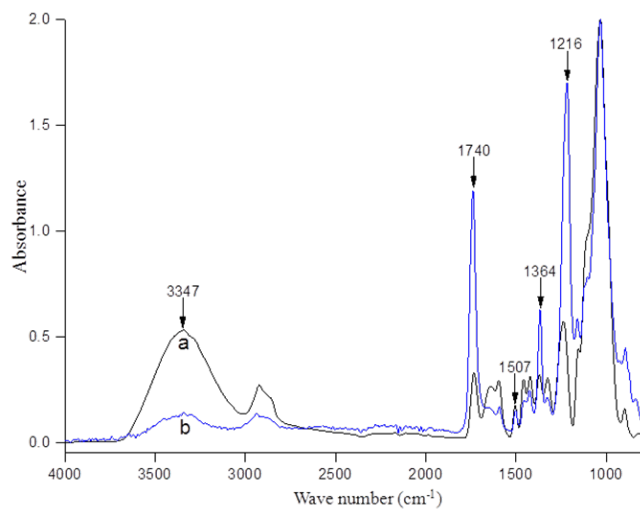
## RESULTS AND DISCUSSIONS

Reaction between IPA and wood in absence of any catalyst (I-0) is insignificant. Figure 2 shows the effect of iodine concentration on weight percent gain (WPG) of modified wood.



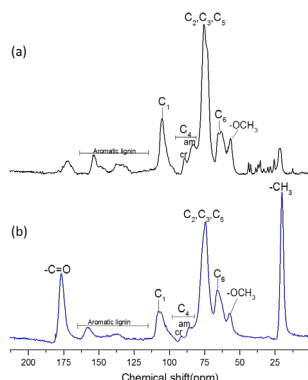
**Figure 2.** Plot of WPG versus reaction time for IPA modified rubber wood at 95°C. Catalyst (iodine) concentrations are: I-0 = 0 mol L<sup>-1</sup>; I-1 = 0,02 mol L<sup>-1</sup>; and I-2 = 0,035 mol L<sup>-1</sup>.

The average WPG increased with increasing reaction time. Samples up to weight gains of 17 % were obtained using to 0,035 mol L<sup>-1</sup> (I-2) of iodine. This WPG value compares well with acetylation of wood using acetic anhydride and corresponds to the level of modification necessary for exhibiting good dimensional stability and durability (Rowell 1983, 2006, 2013).



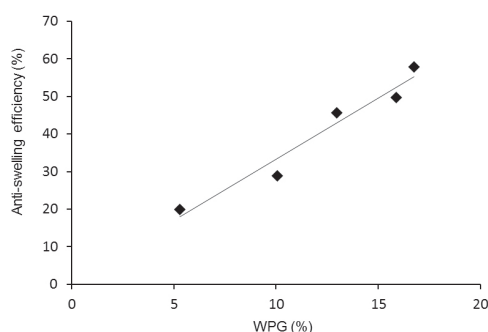
**Figure 3.** FTIR Spectra of unmodified (a) and modified (b) rubber wood.

FTIR spectra of unmodified and modified rubberwood are shown in Figure 3. The FTIR spectra of unmodified wood shows strong O-H stretching absorption at  $3347\text{ cm}^{-1}$  and several other well defined peaks due to various functional groups present in cellulose, hemicelluloses and lignin (Harrington *et al.* 1964, Faix 1992, Pandey 1999). A significant decrease in the O-H stretching band at  $3347\text{ cm}^{-1}$  with a corresponding increase in the C=O stretching absorbance at  $1740\text{ cm}^{-1}$  and C-O stretching at  $1216\text{ cm}^{-1}$  indicates esterification of wood.



**Figure 4.** NMR Spectra of unmodified (a) and modified (b) rubber wood.

The modified wood was further characterized by  $^{13}\text{C}$  CPMAS NMR (Figure 4). The occurrence of two strong signals at 22,7 and 176,1 ppm in modified wood confirms esterification of wood by IPA. The signal at 22,7 is characteristic of a methyl ( $-\text{CH}_3$ ) carbon of the acetyl group and a signal at 176,1 ppm arises due to carbonyl ( $-\text{C}=\text{O}$ ) carbon of acetyl group of acetylated wood (Sun *et al.* 2004).



**Figure 5.** Anti-swelling efficiency (ASE) versus WPG for IPA modified wood using iodine catalyst.

The dimensional stability of modified wood was determined by estimating the volumetric swelling coefficient (S) and anti-shrink/anti-swell efficiency (ASE), using the repeated water-soaking method (Rowell and Ellis 1978). After modification, the volumetric swelling coefficient of modified wood was reduced significantly. The values of ASE after first water soaking cycle against weight gain are plotted in Figure 5. Modified wood exhibited a high ASE value which increases with increase in WPG values. Anti-Swelling Efficiency up to ~ 60% was obtained corresponding to WPG values of ~17%. This indicates high dimensional stability of IPA modified wood.

Above results indicate that iodine is a good catalyst for chemical modification of wood using IPA. The modified wood has high dimensional stability. Modification with IPA may have advantages since there is no acid byproduct.

## CONCLUSIONS

A process of acetylation of solid wood with IPA in presence of iodine has been reported. A high level of modification (~ 17% WPG) was achieved. The average WPG increased with increasing reaction time and catalyst concentration. Modified wood exhibited high dimensional stability.

## ACKNOWLEDGEMENT

This research was supported by CSIR New Delhi (Grant No. 38(1357)/13/EMR (II)).

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