International Scientific Publications: Materials, Methods and Technologies, Vol. 2
ISSN 1313-2539

THE SORPTION OF WATER VAPOUR OF ELM WOOD CHEMICALLY MODIFIED WITH ACETIC OR MALEIC ANHYDRIDE

Antonios Papadopoulos, Ioannis Takos and Dimitrios Emmanouloudis

Technological Educational Institute of Kavala, Department of Forestry and Management of Natural Environment, 66100, Drama, Greece. E-mail antonios1974@hotmail.com, antpap@teikav.edu.gr

Abstract

Elm wood was esterified with acetic and maleic anhydride and studied for moisture adsorption behaviour. The sorption isotherms for untreated and chemically modified wood were analysed using the Hailwood-Horrobin model. The experimental analysis of the sorption isotherms showed that esterification affects total, polymolecular, and monomol-ecular sorption. Acetic anhydride treatment was found more effective in reducing the hygroscopicity of wood compared to maleic anhydride treatment at comparable weight percentage gain.

Key words: *Chemical modification, Acetic anhydride, Maleic anhydride, Sorption, Hailwood-Horrobin model*

1. INTRODUCTION

The fibrous nature of wood has made it one of the most appropriate and versatile raw materials for a variety of uses. However, two properties restrict its much wider use: dimensional changes when subjected to fluctuating humidity, and susceptibility to biodegradation by microorganisms. The varying moisture content of wood results in dimensional and conformational instability, which can compromise the performance of other materials combined with wood, such as adhesives and surface coatings. Until relatively recently, these shortcomings were addressed by impregnating wood with appropriate hydrophobes (Stamm 1964; Kumar 1994). It has now been demonstrated that wood may be modified chemically so that selected properties are enhanced in a more or less permanent fashion (Rowell 1983, Hill and Papadopoulos, 2002).

It has been shown that the dimensional stability of wood can be effectively improved by esterification with anhydrides (Rowell *et al*. 1988, Papadopoulos and Hill, 2003). There is limited work reported on the water vapour sorptive properties of such modified woods. A number of authors have investigated the sorption isotherms of acetylated wood specimens at only one level of substitution (Risi and Arseneau 1957; Spalt 1958; Popper and Bariska 1972; Yasuda *et al*. 1995).

In this study, water adsorption behaviour of one widely used Greek hardwood, namely elm (*Ulmus montana)*, esterified by acetic and maleic anhydride was investigated. Esterified wood was analysed by FTIR spectroscopic technique to study the changes in spectral intensity of hydroxyl groups of cell wall polymers during the reaction with anhydrides. Adsorption isotherms were obtained to assess the hygroscopicity of esterified wood, using the Hailwood-Horrobin sorption theory.

2. EXPERIMENTAL

Wood modification reactions

Sapwood samples of dimension 20 mm x 20 mm x 5 mm (radial x tangential x longitudinal) were cut from freshly-felled kiln-dried elm (*Ulmus Montana*). Samples were carefully smoothed with sandpaper to remove loosely adhering fibres, then placed in a Soxhlet extractor for solvent extraction using toluene/methanol/acetone (4:1:1 by volume) for 8 h. and subsequently dried in an oven for 8 h at

ISSN 1313-2539

105oC. Samples were removed from the oven, transferred to a vacuum desiccator and allowed to cool to ambient temperature over silica gel. Prior to reaction, each sample was weighed on a four-figure balance. Samples (thirty replicates) were then vacuum impregnated with pyridine (dried over KOH) for 1 h, then transferred to a flask containing pyridine set in an oil bath at 100oC. Samples were allowed to equilibrate in the hot pyridine for one hour. After heating for 1 h, the sample batch was transferred to a round-bottom flask containing a one molar solution of the anhydride (acetic or maleic) in pyridine set in an oil bath at 100oC. At the end of the reaction period (5 hours), the flask was removed from the oil bath, the hot reagent decanted off, and ice cold acetone added to quench the reaction. Samples were kept in the acetone for 1 h, before being transferred to the Soxhlet apparatus for solvent extraction, as previously detailed. Samples were then oven dried at 105oC for 8 h and weight gain due to reaction recorded.

Infra-red (IR) Analysis

For Infra-red (IR) analysis, the treated samples were ground up by using a microdismembrator (20.000 rpm for 6 min). The fibre flour was then mixed with oven- dry potassium bromide (KBr) powder (the fibre flour/KBr ratio was 1:100) and placed in a vibratory ball mill capsule. The mixture was ground for about 2 min. The ground mixture was then transferred to a press and the bolts of press screwed down. The bolts were tightened with a spanner to press the disk. After a few minutes, the bolts were loosen and removed. The press was placed directly into a sample beam of a Mattson FTIR spectrometer, Nicolet 750, series II.

Determination of moisture adsorption isotherms

Test samples were kept above saturated solutions of various salts in containers stored in a controlled temperature room set at 20oC (variation +/- 1oC). Six salts were chosen and these are listed in Table 1, along with the RH of the atmosphere above each saturated solution at 20oC (according to Kaye and Laby 1973). They were chosen on the basis of giving minimum RH variation with changes in the temperature (Stamm 1964). Data published by Kaye and Laby (1973) show the equilibrium RH above saturated solutions of these salts to be insensitive to any variation in temperature expected in the controlled temperature room (a variation around 20oC of +/-5oC, causing a maximum variation of +/- 1% RH). Excess salt was always present within each solution to ensure saturation was maintained. The solution and air in the container were agitated by bubbling air through the solution. The oven-dry wood samples were placed in the containers above saturated salt solutions. They were left to equilibrate for 4 weeks and then weighed once a week, using a four-place analytical balance, until it became obvious that no significant weight change had occurred since the last weight was recorded (and equilibrium moisture content (EMC) had been attained). After the adsorption equilibrium was attained, samples were weighed, and the moisture content was calculated on the oven dried weight basis.

Table 1. Saturated salt solutions used and their resultant relative humidities at 20 0C.

Salt	RH (%)
Potassium nitrate (KNO3)	93
Sodium chloride (NaCl)	76
Sodium dichromate (Na2Cr2O7)	55
Potassium carbonate (K2CO3)	44
Potassium acetate (CH3COOK)	23
Lithium chloride (LiCl)	12

ISSN 1313-2539

3. RESULTS AND DISCUSSION

Infra-red (IR) Analysis

Esterification of wood was established by infra-red spectroscopy (Fig. 1). Infra-red spectra confirmed the occurrence of wood-anhydride reaction. The strong vibrational absorbance obtained in the region of 1736 and 1730cm-1 (C=O) was a distinct pattern present in modified samples, which indicates ester bond formation. As expected, such absorption was not present in unmodified wood.

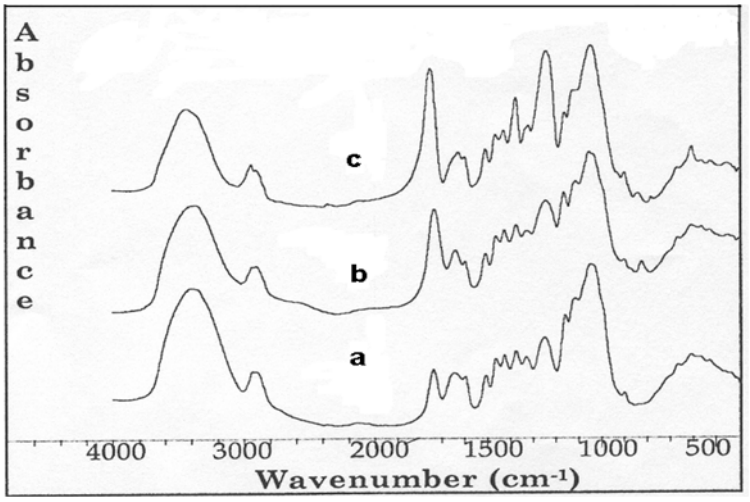


Fig. 1. FTIR spectra of esterified and control wood: (a) control, (b) modified with maleic anhydride and (c) modified with acetic anhydride.

Moisture adsorption isotherms

Isotherm fitting

To the experimental mean (average values obtained from two replicate samples) moisture contents at each RH values, the Hailwood-Horrobin (1946) adsorption equation was applied. The adsorption equation is defined as follows:

$$h/M = A + Bh - Ch2, \quad (1)$$

where:

$$A = \frac{W}{18}\left[\frac{1}{K_2(K_1+1)}\right] \quad (2)$$

$$B = \left(\frac{W}{1{,}800}\right)\left[\frac{K_1-1}{K_1+1}\right] \quad (3)$$

ISSN 1313-2539

$$C = \left(\frac{W}{180{,}000}\right)\left[\frac{K_1 K_2}{K_1 + 1}\right] \quad (4)$$

h (%) is RH, M (%) is moisture content, $K1$ is the equilibrium constant where the hydrate is formed from dissolved water and dry wood, $K2$ is the equilibrium constant between dissolved water and water vapour and W is the molecular weight of dry wood polymer per mole of water sorption sites. The H-H model divides total moisture sorbed into its monomolecular and polymolecular components. The equation for the model is as follows:

$$M = Mh + Md = \frac{1{,}800}{W}\left(\frac{K_1 K_2 h}{100 + K_1 K_2 h}\right) + \frac{1{,}800}{W}\left(\frac{K_2 h}{100 - K_2 h}\right) \quad (5)$$

where:

M is the wood moisture content in equilibrium with h, Mh is the moisture content relating to the hydrate water (monomolecular sorption), and Md is the moisture content relating to the dissolved water (polymolecular sorption).

From Equation 1 it can be seen that the H-H theory predicts a parabolic relationship between the ratio h/M and h. The constants A, B and C are obtained from the fitting parameters of a second-order polynomial. From these parameters the values of $K1$, $K2$ and W can be calculated as follows:

$$K_1 = 1 + \frac{B^2 + \sqrt{B^2 + 4AC}}{2AC} \quad (6)$$

$$K_2 = \frac{200C}{B + \sqrt{B^2 + 4AC}} \quad (7)$$

$$W = 1800\left(\frac{4AC + B^2 + B\sqrt{B^2 + 4AC}}{B + \sqrt{B^2 + 4AC}}\right) \quad (8)$$

The values of A, B, C, coefficient of determination (R2), $K1$, $K2$ and W of various modified woods are presented in Table 2. The degree of fit, as measured by the coefficient of determination (R2) is remarkably high, considering the complexity of the matrix of data, where wood samples were chemically modified at several levels of reaction with different anhydrides. The R2 values range from 0.844 to 0.981, indicating good fit to the experimental results. R2 is a statistical measure of the proportion of variation that can be explained by the regression line (*i.e.* for unmodified control maple wood, the regression line accounted for 98.1% of variation); the lower the R2 value, the lower the proportion of total variation accounted for the fitted regression line. The physical constants $K1$, $K2$, W obtained were found to be in good agreement with those previously reported by Spalt (1958) and Wangaard and Granados (1967) for unmodified wood, and by Spalt (1958) for acetylated wood. For the modified wood, the W values increase as the WPG increases, indicating that a proportion of sites are made unavailable for water sorption.

ISSN 1313-2539

Table 2. Fitted and physical constants calculated for the Hailwood –Horrobin adsorption isotherms.

Reagent	WPG	A	B	C	K1	K2	Wo	R2
Elm wood								
Control	0	3,58	10,78	10,27	4,95	0,76	292,0	0.981
Acetic	14.1	8,21	12,95	14,64	3,06	0,76	458,3	0.884
Maleic	15.9	5,99	12,47	12,84	3,75	0,75	387,3	0.844

As defined above, the constant *K2* expresses the activity of dissolved water per unit relative vapour pressure. According to Okoh and Skaar (1980), its value should be unity if it has the same activity as liquid water. The *K2* values vary approximately between 0.75 and 0.76, indicating that the dissolved water shows a lower activity than the liquid water. This suggests that the freedom of motion of water in the cell wall micropores (dissolved water) is not the same as that in liquid water.

Adsorption isotherms are shown in Fig. 2. Equilibrium moisture content of modified wood was reduced at all relative humidities compared to the control, indicating a reduction in the hygroscopicity of wood. The adsorbed water was then separated into hydrate water relating to monomolecular sorption and into dissolved water relating to polymolecular sorption, using the Equation (5). The isotherms for monomolecular and polymolecular adsorption are plotted in Figures 3, indicating a reduction in the hygroscopicity of wood at both the monomolecular and the polymolecular level.

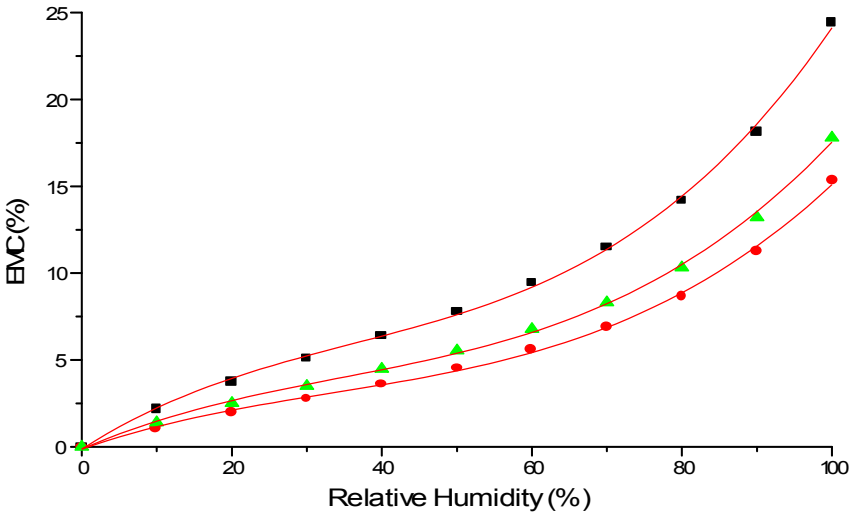


Fig. 2. Adsorption isotherms for unmodified (■), modified with acetic (●) and maleic (▲) anhydride elm wood.

ISSN 1313-2539

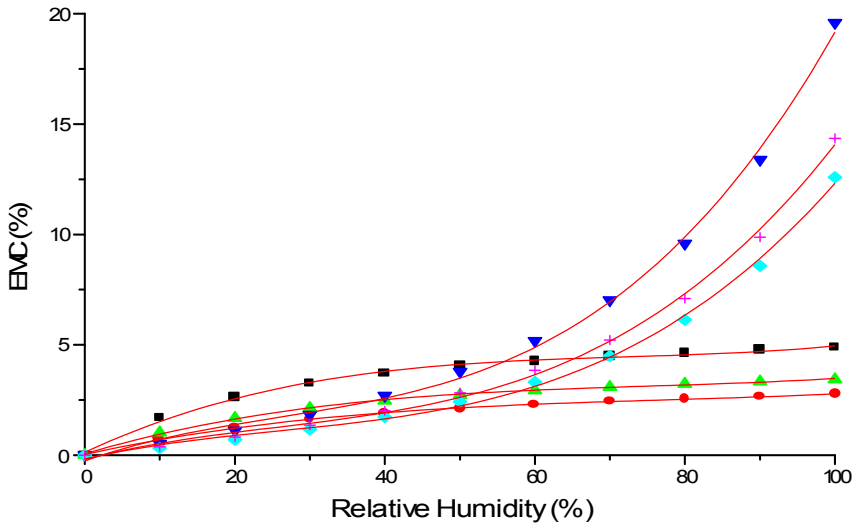


Fig. 3. Polymolecular adsorption isotherms for unmodified, modified with acetic, maleic (+) anhydride elm wood and monomolecular adsorption isotherms for unmodified, modified with acetic, maleic anhydride elm wood.

Acetic anhydride treatment was found to be more effective in reducing the hygroscopicity of wood, compared to maleic anhydride treatment at comparable weight percentage gain, at the total, monomolecular, and polymolecular levels, as it can been seen in Fig. 2 and 3. This is perhaps illustrated more clearly in Table 3, which presents the reduction in the hygroscopicity at saturation. It can be seen that the esterification with acetic anhydride to elm wood reduced total sorption by 38%, polymolecular sorption by 35.8%, and monomolecular sorption by 44% at saturation, whereas the corresponding reduction due to maleic anhydride was lower for both total, monomolecular and polymolecular level. The better performance of wood modified with acetic anhydride may be attributed to the smaller anhydride molecule, since it was known that the micropore network geometry controls the accessibility of molecules to the cell wall interior (Hill and Papadopoulos, 2001). It is resonable therefore to expect that different sized molecules would have different accessibility to the cell wall.

Table 3. Reduction in the hygroscopicity (%) at saturation of maple and elm wood as a result of esterification with acetic and maleic anhydride.

Reagent	**WPG**	**Reduction in Hygroscopicity (%)**		
		Total	Polymolecular	Monomolecular
Elm wood				
Acetic	15.3	38	35.8	44
Maleic	16.3	27.1	26.1	29.8

ISSN 1313-2539

The efficacy of modified wood with different anhydrides in reducing hygroscopicity has been the subject of many studies. A comprehensive investigation into the effect of molecular size of the substituent group of softwood modified with linear chain carboxylic acid anhydrides, namely acetic, propionic, butyric, valeric, hexanoic, upon the sorption of water vapour has been performed (Papadopoulos and Hill, 2003). Analysis of the sorption isotherms, using the Hailwood-Horrobin model, at comparable weight percentage gain, revealed that the five anhydrides used show similar effectiveness in total, polymolecular and monomolecular sorption, despite the substantial differences in the proportion of hydroxyl groups reacted. It was concluded that the reduction in total, polymolecular, and monomolecular sorption produced by the linear chain anhydrides is primarily determined by the volume of adduct deposited in the cell wall (bulking), rather than by the number of hydroxyl groups which have been substituted. The sorption properties of modified white fir with acetic and phthalic anhydride were measured by fitting isotherms to sorption data using the BET and Hailwood–Horrobin models (Popper and Bariska, 1972). It was found that the reaction with acetic anhydride significantly reduced monomolecular adsorption, as the hydrophilic hydroxyl groups were replaced. In contrast, wood modified with phthalic anhydride gave monomolecular adsorption isotherms similar to untreated wood. This was attributed to the hydrophilic acid introduced during reaction with phthalic anhydride. Similar observation was also made by Chauhan *et al.* (2001) in rubber wood. In this case, not much difference was observed in the behaviour of maleic and phthalic anhydride treated wood.

4. CONCLUSIONS

1. Water vapour sorption isotherms for untreated and chemically modified wood were analysed using the Hailwood-Horrobin model. The experimental analysis of the sorption isotherms showed that esterification affects the total, polymolecular, and monomolecular sorption.
2. Acetic anhydride treatment was found to be more effective in reducing the hygroscopicity of wood, compared to maleic anhydride treatment at comparable weight percentage gain.

REFERENCES

Chauhan, S. S., Aggrawal, P., Karmarkar, A., and Pandey, K. K. (2001). "Moisture adsorption behaviour of esterified rubber wood (*Hevea brasiliensis)*," *Holz als Roh-und Werkstoff* 59, 250-253.

Hailwood, A. J., and Horrobin, S. (1946). "Absorption of water by polymers: Analysis in terms of a simple model," *Trans. Faraday Soc*. 42 B, 84-92; 93-102.

HILL C.A.S AND A.N. PAPADOPOULOS (2001). A REVIEW OF METHODS USED TO DETERMINE THE SIZE OF THE CELL WALL MICROVOIDS OF WOOD. *JOURNAL OF THE INSTITUTE OF WOOD SCIENCE* 15(6):337-345.

HILL, C. A. S., AND PAPADOPOULOS, A. N. (2002). "THE PYRIDINE CATALYSED ACYLATION OF SAPWOOD AND PHENOLIC MODEL COMPOUNDS WITH CARBOXYLIC ACID ANHYDRIDES. DETERMINATION OF ACTIVATION ENERGIES AND ENTROPY OF ACTIVATION," *HOLZFORSCHUNG* 56, 150-156.

Hill, C. A. S., Jones, D. (1996). "The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. The effect of chain length," *Holzforschung* 50, 457-462.

Kaye, G. W. C., and Laby, T. H. (1966). *Tables of physical and chemical constants and some mathematical functions.* Longmans, London.

Kumar, S. (1994). "Chemical modification of wood," *Wood and Fiber Sci*. 26, 270-280.

ISSN 1313-2539

Okoh, K. I. A., and Skaar, C. (1980). "Moisture sorption isotherms of the wood and inner bark of the southern U.S. hardwoods," *Wood and Fiber Sci.* 12, 98-111.

Papadopoulos, A. N., and Hill, C. A. S. (2003). "The sorption of water vapour by anhydride modified softwood," *Wood Sci. Technol*. 37, 221-231.

Popper, R., and Bariska, M. (1972). "Acylation of wood. Part I: The sorption behaviour of water vapour," *Holz als roh-und Werkstoff* 30, 289-294.

Risi, J., and Arseneau, D. F. (1957). "Dimensional stabilisation of wood. Part I: Acetylation," *Forest Prod J.* 7, 210-213.

Rowell, R. M. (1983). "Chemical modification of wood," *For. Prod. Abstr*. 6, 366-382.

Rowell, R. M., Youngquist, J. A., and Montrey, H. M. (1988). "Chemical modification: adding value through new FPL composite technology," *Forest Prod. J*. 38, 67-70.

Spalt, H. A. (1958). "The fundamentals of water vapour sorption by wood." *Forest Prod. J.* 8, 258-295.

Stamm, A. J. (1964). *Wood and Cellulose Science*, Ronald Press Co., New York.

Wangaard, F. F., and Granados, L. A. (1967). "The effect of extractives on water-vapour sorption by wood," *Wood Sci. Technol*. 1, 253-277.

Yasuda, R., Minato, K., and Norimoto, M. (1995). "Moisture adsorption thermodynamics of chemically modified wood," *Holzforshung* 49, 548-554.