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Moisture adsorption isotherms of two esterified Greek hardwoods

Abstract Two Greek hardwoods (*Ulmus montana* and *Acer pseudoplatanus*), were 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 both total, polymolecular and monomolecular sorption. Acetic anhydride treatment was found more effective in reducing the hygroscopicity of wood compared to maleic anhydride treatment at comparable weight percentage gain, reflecting probably the strong ester bonds between acetic anhydride and wood. Identical e.m.c values were attained in both types of sorption for maple and elm wood, at comparable weight percentage gain, not only for the unmodified samples but for the modified ones as well.

Sorptionsisothermen von zwei veresterten griechischen Laubhölzern

Zusammenfassung Zwei griechische Laubhölzer (*Ulmus montana* und *Acer pseudoplatanus*) wurden mit Acet- und Maleinanhydrid verestert und ihr Feuchte-Sorptionsverhalten untsersucht. Die Sorptionsisothermen der unbehandelten und chemisch behandelten Proben wurden mittels des Hailwood-Horrobin-Modells analysiert. Es zeigte sich, dass die Veresterung sowohl die polymolekulare als auch die monomolekulare Sorption beeinflusst. Die Behandlung mit Acetanhydrid war bei vergleichbarem Massenzuwachs effektiver als mit Maleinanhydrid bezüglich des Erniedrigens der hygroskopischen Eigenschaft, was wahrscheinlich mit den starken Esterbindungen zwischen Holz und Acetanhydrid zusammenhängt. Die Gleichgewichtsfeuchten waren bei vergleichbaren Gewichtszunahmen für beide Holzarten und beide Sorptionstypen identisch, und zwar nicht nur für die unbehandelten, sondern auch für die modifizierten Proben.

Keywords Chemical modification · Esterification · Hailwood-Horrobin model · Sorption · Greek wood species

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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). Although the effect on overall stabilisation in response to liquid water soaking is well documented (Stamm 1964; Rowell 1983; Hill and Jones 1996), there is little evidence of how sorption is influenced by esterification with anhydrides. Recently, a

124

comprehensive investigation into the water sorptive properties and into the effect of molecular size of the substituent group upon the sorption of water vapour of softwood modified with linear chain carboxylic acid anhydrides was carried out, using the Hailwood–Horrobin model (Papadopoulos and Hill 2003). It was concluded that the reduction in total, polymolecular and monomolecular adsorption 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.

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

2 Experimental

2.1 Wood modification reactions

Sapwood samples of dimension 20×20×5 mm (radial× tangential×longitudinal) were cut from freshly felled kiln dried elm and maple. 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 105°C. 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 (30 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 100°C. Samples were allowed to equilibrate in the hot pyridine for 1 h. 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 100°C. At the end of the reaction period (5 h), 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 105°C for 8 h and weight gain due to reaction recorded.

2.2 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.

2.3 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 20°C (variation ±1°C). Six salts were chosen and these are listed in Table 1, along with the RH of the atmosphere above each saturated solution at 20°C (according to Kaye and Laby 1966). They were chosen on the basis of giving minimum RH variation with changes in the temperature (Stamm 1964). Data published by Kaye and Laby (1966) 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 20°C of ±5°C 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 moisture content was calculated on the oven dried weight basis.

3 Results and discussion

3.1 Infra-red (IR) analysis

Esterification of wood was established by infra-red spectroscopy (Fig. 1). Infra-red spectra confirmed the

Table 1 Saturated salt solutions used and their resultant relative humidities at 20°C
Tabelle 1 Gesättigte Salzlösungen und ihre Endfeuchten bei 20°C

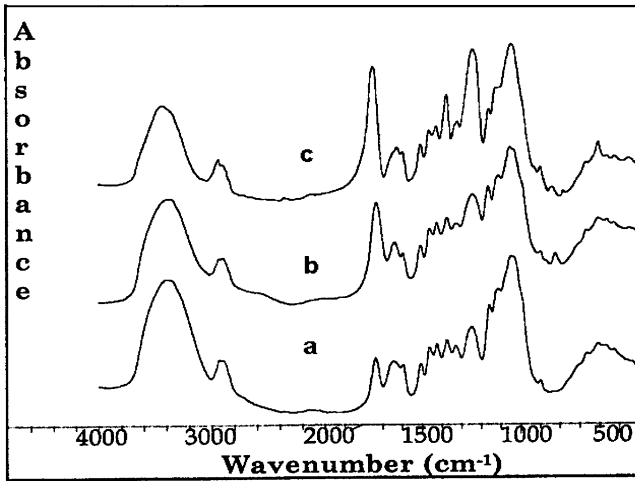| Salt	RH (%)
Potassium nitrate (KNO_3)	93
Sodium chloride (NaCl)	76
Sodium dichromate ($Na_2Cr_2O_7$)	55
Potassium carbonate (K_2CO_3)	44
Potassium acetate (CH_3COOK)	23
Lithium chloride (LiCl)	12

Fig. 1 FTIR spectra of esterified and control wood: **a** control, **b** modified with maleic anhydride and **c** modified with acetic anhydride
Abb. 1 FTIR-Spektren von veresterten und Kontrollproben: (a) Kontrollproben; (b) modifiziert mit Maleinanhydrid; (c) modifiziert mit Acetanhydrid

occurrence of wood-anhydride reaction. The strong vibration obtained in the region of 1736 and 1730 cm^{-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.

3.2 Moisture adsorption isotherms

3.2.1 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:

$$h/M = A + Bh - Ch^2, \qquad (1)$$

where

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

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

$$C = \left(\frac{W}{180,000}\right)\left[\frac{K_1K_2}{K_1+1}\right], \qquad (4)$$

h (%) is RH, M (%) is moisture content, K_1 is the equilibrium constant where the hydrate is formed from dissolved water and dry wood, K_2 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:

$$
\begin{aligned}
M &= M_h + M_d \\
&= \frac{1,800}{W}\left(\frac{K_1K_2h}{100+K_1K_2h}\right) + \frac{1,800}{W}\left(\frac{K_2h}{100-K_2h}\right), \quad (5)
\end{aligned}
$$

where M is the wood moisture content in equilibrium with h, M_h the moisture content relating to the hydrate water (monomolecular sorption), M_d is the moisture content relating to the dissolved water (polymolecular sorption).

From Eq. 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 the second order polynomial. From these parameters the values of K_1, K_2 and W can be calculated as follows:

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

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

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

The values of A, B, C, coefficient of determination (R^2), K_1, K_2 and W of various modified woods are presented in Table 2. The degree of fit, as measured by the coefficient of determination (R^2) 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 R^2 values range from 0.822 to 0.992, indicating good fit to the experimental results. The R^2 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 99.2% of variation); the lower the R^2 value the lower the proportion of total variation accounted for the fitted regression line. The physical constants K_1, K_2, W obtained were found to be

Table 2 Fitted and physical constants calculated for the Hailwood–Horrobin adsorption isotherms
Tabelle 2 Angepasste physikalische Kontanten, berechnet nach dem Sorptionsisothermen-Modell nach Hailwood-Horrobin

Reagent	WPG	A	B	C	K_1	K_2	W_o	R^2
Maple wood								
Control	0	3.22	11.46	10.57	5.68	0.76	294.3	0.992
Acetic	15.3	7.73	13.38	13.88	3.37	0.72	443.9	0.851
Maleic	16.3	5.58	13.18	12.83	4.18	0.74	386.0	0.822
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

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.

As defined above, the constant K_2 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 K_2 values vary approximately between 0.72 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 Figs. 2 and 3, for maple and elm wood respectively. 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 Eq. 5. The isotherms for monomolecular and polymolecular adsorption are plotted, in Figs. 4 and 5 for maple and elm wood respectively, indicating a reduction in the hygroscopicity of wood at both monomolecular and polymolecular level.

Acetic anhydride treatment is found more effective in reducing the hygroscopicity of wood compared to maleic anhydride treatment at comparable weight percentage gain, at both total, monomolecular and polymolecular level, as it can been seen in Figs. 2–5. 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
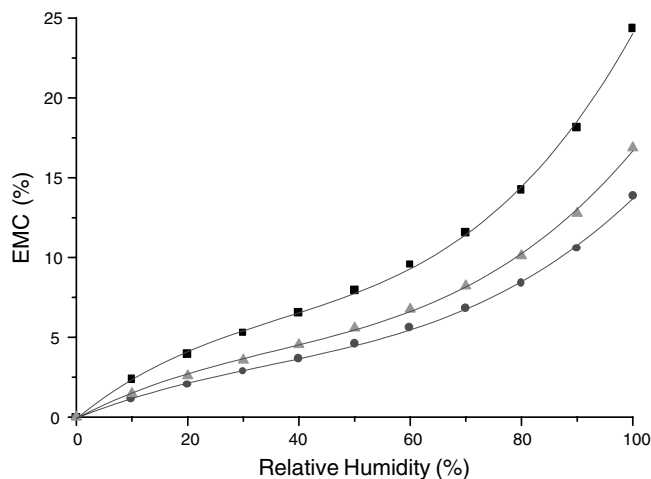

Fig. 3 Polymolecular adsorption isotherms for unmodified (*filled square*), modified with acetic (*filled inverted triangle*), maleic (+) anhydride maple wood and monomolecular adsorption isotherms for unmodified (*open square*), modified with acetic (*filled triangle*), maleic (*open triangle*) anhydride maple wood
Abb. 3 Polymolekulare Sorptionsisothermen für unmodifizierte Ahornproben (*filled square*), modifiziert mit Acetanhydrid (*filled inverted triangle*), mit Maleinanhydrid (+) sowie monomoleculare Sorptionsisothermen für unmodifizierte Ahornproben (*open square*), modifiziert mit Acet- (*filled triangle*) und Maleinanhydrid (*open triangle*)

maple wood was to reduce total sorption by 41.7%, polymolecular sorption by 41.3% and monomolecular sorption by 42.5% at saturation, whereas the corresponding reduction due to maleic anhydride was 29.4% at both total, monomolecular and polymolecular level. This holds also for the elm wood. The better performance of wood modified with acetic anhydride may be attributed to strong ester bonds between acetic anhydride and wood.

Fig. 2 Adsorption isotherms for unmodified (*open square*), modified with acetic (*filled square*) and maleic (*filled triangle*) anhydride maple wood
Abb. 2 Sorptionsisothermen für Ahornproben: unmodifiziert (*open square*), modifiziert mit Acet- (*filled square*) und Maleinanhydrid (*filled triangle*)
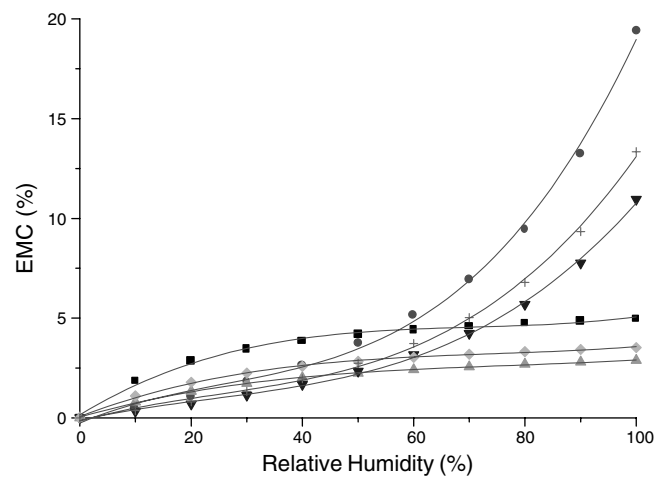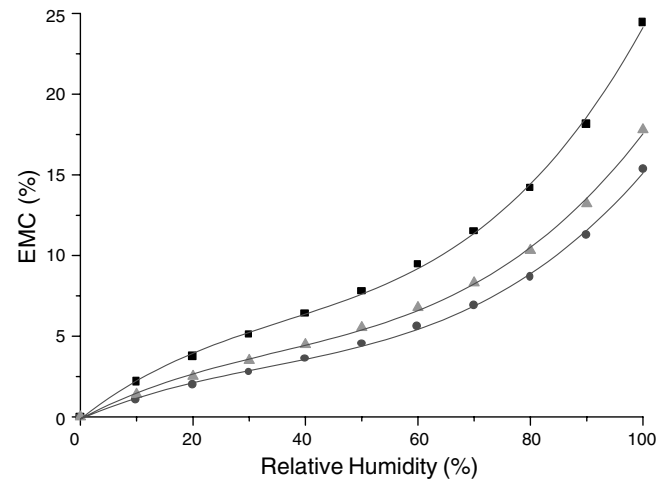

Fig. 4 Adsorption isotherms for unmodified (*open square*), modified with acetic (*filled square*) and maleic (*filled triangle*) anhydride elm wood
Abb. 4 Sorptionsisothermen für unmodifizierte Ulmenproben (*open square*), modifiziert mit Acet- (*filled square*) and Maleinanhydrid (*filled triangle*)
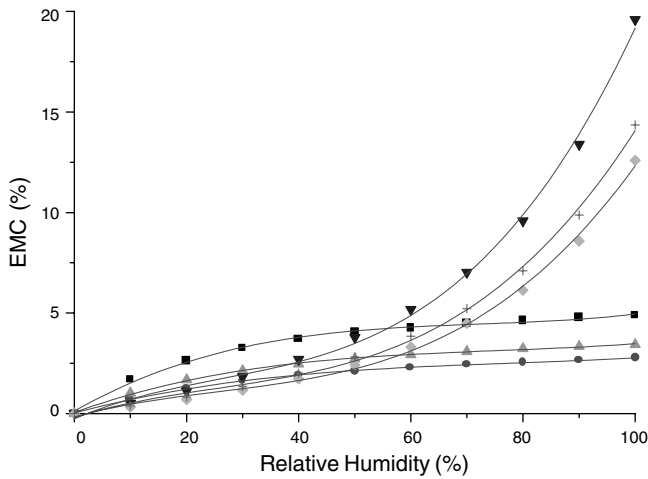
Fig. 5 Polymolecular adsorption isotherms for unmodified (*filled inverted triangle*), modified with acetic (*open triangle*), maleic (+) anhydride maple wood and monomolecular adsorption isotherms for unmodified (*open square*), modified with acetic (*filled square*), maleic (*filled triangle*) anhydride maple wood
Abb. 5 Polymolekulare Sorptionsisothermen für unmodifizierte Ahornproben (*filled inverted triangle*), modifiziert mit Acet- (*open triangle*), und Maleinanhydrid (+) sowie monomolekulare Sorptionsisothermen für unmodifiziertes Ahornholz (*open square*), modifiziert mit Acet- (*filled square*) und Maleinanhydrid (*filled triangle*)
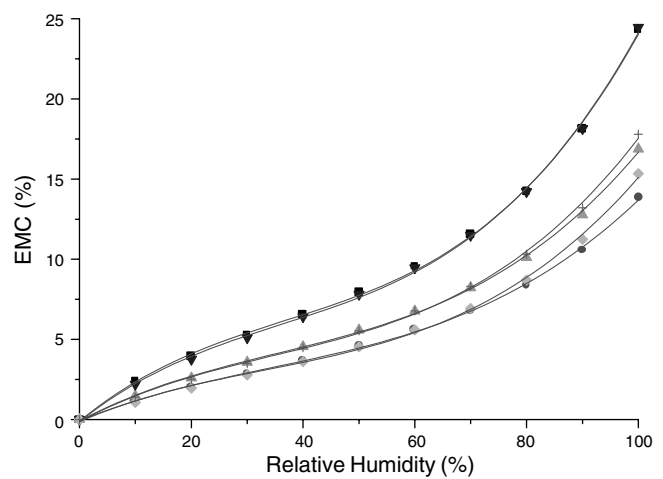

Fig. 6 Adsorption isotherms for unmodified (*open square*), modified with acetic (*filled square*), maleic (*filled triangle*) anhydride maple wood and for unmodified (*filled inverted triangle*), modified with acetic (*open triangle*), maleic (+) anhydride elm wood
Abb. 6 Sorptionsisothermen für unmodifiziertes Ahornholz (*open square*), modifiziert mit Acet- (*filled square*) und Maleinanhydrid (*filled triangle*) sowie für unmodifiziertes Ulmenholz (*filled inverted triangle*), modifiziert mit Acet- (*open triangle*) und Maleinanhydrid (+)

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 both total, polymolecular and monomolecular sorption, despite the substantial difference 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

Table 3 Reduction in the hygroscopicity (%) at saturation of maple and elm wood as a result of esterification with acetic and maleic anhydride
Tabelle 3 Herabsetzen der hygroskopischen Eigenschaft (in%) bei Sättigung von Ahorn- und Ulmenholz nach Veresterung mit Acet- und Maleinanhydrid

Reagent	WPG	Reduction in hygroscopicity (%)		
		Total	Polymolecular	Monomolecular
Maple wood				
Acetic	15.3	41.7	41.3	42.5
Maleic	16.3	29.4	29.4	29.4
Elm wood				
Acetic	15.3	38	35.8	44
Maleic	16.3	27.1	26.1	29.8

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 hydroxyl 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.

The effect of modification on hygroscopicity on two substrates used in this study, namely maple and elm, has been compared in Fig. 6. It is revealed that the e.m.c values attained are identical for the two substrates, not only for the unmodified samples but for the modified ones as well.

4 Conclusions

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 the total, polymolecular and monomolecular sorption. Acetic anhydride treatment was found more effective in

reducing the hygroscopicity of wood compared to maleic anhydride treatment at comparable weight percentage gain, reflecting probably the strong ester bonds between acetic anhydride and wood. Identical e.m.c values were attained in both types of sorption for maple and elm wood, at equivalent WPG, not only for the unmodified samples but for the modified ones as well.

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