

Vapour Sorption Studies of Belmadur Wood

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Abstract

In this study, the water vapour sorption of Belmadur wood is fully investigated. The sorption isotherms were analysed using the Hailwood-Horrobin model. Belmadur wood was shown lower total sorption by 26.5%, polymolecular sorption by 23.9% and monomolecular sorption by 33.1% at saturation, compared with the untreated wood. Regression analysis of the EMC values at saturation revealed that the variation shown in the water sorbed at the polymolecular level plays the main role in the variation in total water sorbed. In addition, it was found that only the reduction in monomolecular sorption can be primarily attributed to the decrease in site accessibility.

Keywords

Modification; Impregnation; Sorption; Belmadur Wood; Hailwood-Horrobin Model; Dmdheu

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). Wood may also be modified so that selected properties are enhanced in a more or less permanent fashion (Rowell 1983). Modification of wood can involve active modifications, which result in a change to a chemical nature of the material, or passive modifications, where a change in properties is effected, but without an alteration of the chemistry of the material (Hill 2006). Modification methods can be classified as follows: chemical, thermal,

surface and impregnation modification. Most of the chemical modification methods investigated to date have involved the chemical reaction of a reagent with the cell wall polymer hydroxyl groups (OH). This can result in the formation of a single chemical bond with one OH group, or cross linking between two or more OH groups. The chemical nature of the cell wall polymers is thus changed, which may be responsible for new properties. Thermal modification of wood is defined as the application of heat to wood in order to bring about a desired improvement in the performance of the material. The surface modification of wood is defined as the application of a chemical, physical or biological agent to the wood surface in order to effect a desired performance of the material. On the other hand, impregnation of wood cell wall with chemicals of various types is a very broad area. In most studies, the impregnation involves the treating of wood with a monomer solution that diffuses into the cell wall, followed by subsequent polymerisation. Property improvements occur primarily due to bulking of the cell wall by the impregnant. Therefore, impregnation modification can be defined as any method that results in the filling of the wood substance with an inert material (impregnant) in order to bring about a desired performance change (Hill 2006). As with so many research areas in impregnation modification, much of the early work in resin modification was performed by Alfred Stamm and co-workers at the forest Products Laboratory in Madison (Stamm and Seborg 1941). On the basis of this work, two veneer-based products were developed (Impreg and Compreg), by using commercial resins (phenol formaldehyde, urea and thiourea). Unlike the commercial resins, dimethylol-dihydroxy-ethylene urea (DMDHEU), is a resin that was developed for the textile rather than the wood processing industry. Weaver et al. (1961) appear to have been the first researchers to have studied the modification of wood with this compound, finding

rather poor dimensional stabilisation. Nicholas and Williams (1987) studied the use of DMDHEU to improve the dimensional stability of wood. They investigated the effect of different curing agents and temperatures upon the dimensional and strength properties of wood specimens. In most cases, although treatments imparted varying degrees of dimensional stability, there was a large reduction in modulus of rupture. Militz (1993) tested beech wood treated with DMDHEU and evaluated the effectiveness of a variety of commercial catalysts. It was found that temperatures of 100°C were necessary for the effective curing of the resin. The ASE value (anti-shrink efficiency) was 75%.

A commercial technology, based on the impregnation modification of wood, is the Belmadur technology. Belmadur technology is claimed to be an innovative modification process under which the wood is impregnated under pressure and cross-linked by curing. The technology is based on very simple process steps. The first stage consists of penetrating the wood with a proprietary DMDHEU solution, that is, an aqueous solution of a cross-linking agent (Militz 1993). The air is removed from the cell structure by applying a vacuum to ensure that the cross-linking agent can reach the innermost cells when the solution is applied under pressure. The next stage consists of drying the impregnated wood at a temperature of more than 100°C. This causes the cross-linking agent molecules to cure by polycondensation and water is released (Krause and Militz 2009). The purpose of this paper is to investigate the water vapour sorption of Belmadur wood. Several models for fitting sorption isotherms to empirical data have been proposed. One such model is that introduced by Hailwood and Horrobin (1946). Due to the close fit found when the Hailwood-Horrobin (H-H) single-hydrate model has been applied to equilibrium moisture data for wood (Spalt 1958; Simpson 1980) and for chemically modified wood with linear chain carboxylic acid anhydride reagents (Papadopoulos and Hill 2003), this model was also used in this study. A further advantage of the model is the ease with which the total water sorbed can be attributed to monomolecular and polymolecular sorption. This is potentially of great use when assessing and comparing wood treated with a variety of chemicals. Furthermore, the H-H model does not require any assumptions to be made regarding the nature of the geometry of the micropores within the cell wall.

Materials and Methods

Belmadur wood samples

The wood samples used in this work were supplied by the company Method SA (Trikala, Greece) which uses three-layer laminated Belmadur pine wood for the production of window frames. Method SA imports Belmadur wood from the industry Adolf Münchinger GmbH & Co. KG (Leutershausen, Germany), which has the use rights of the technology. The three-layer laminated samples were consisted from the outer wood layer which was treated Belmadur and two inner layers of untreated pine wood. Wood samples of Belmadur and untreated Scots pine wood (*Pinus sylvestris* L) with air dry densities of 0.560 and 0.480 g/cm³ respectively, were used in this study, as supplied with no further treatment.

Determination of moisture sorption isotherms

The method for controlling the relative humidity (RH) as described by Stamm (1964), has been widely used and was selected for being simple, economical and reasonably precise. Test samples of dimension 20 mm x 20 mm x 10 mm (radial x tangential x longitudinal) were kept above saturated solutions of various salts in containers stored in a controlled temperature room set at 20°C (variation +/- 1°C). Pure water results in the saturated vapour pressure corresponding to 100% RH. The addition of a solute to water reduces its vapour pressure in proportion to its mole fraction in the case of diluted solutions. When a saturated solution at a controlled temperature is used, a constant RH is maintained (Siau 1984).

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 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 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.

Results and Discussion

Isotherm fitting

The mean (average values obtained from ten replicate samples) moisture contents at each RH of various modified woods are given in Table 2. To the experimental mean values, the H-H (1946) adsorption equation was applied. The adsorption equation is defined as follows:

$$h/M = A + Bh - Ch^2, \tag{1}$$

where:

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

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

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

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:

$$M = M_h + M_d = \frac{1,800}{W} \left(\frac{K_1 K_2 h}{100 + K_1 K_2 h} \right) + \frac{1,800}{W} \left(\frac{K_2 h}{100 - K_2 h} \right) \tag{5}$$

Where:

M is the wood moisture content in equilibrium with h , M_h is the moisture content relating to the hydrate water (monomolecular sorption), M_d 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 the second order polynomial. From these parameters the values of K_1 , K_2 and W can be calculated as follows:

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

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

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

The values of A , B , C , coefficient of determination (R^2), K_1 , K_2 and W of various both treated and untreated wood are presented in Table 3. 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 indicating good fit to the experimental results.

The physical constants K_1 , K_2 , W obtained were found to be in good agreement with those previously reported by Spalt (1958); Wangaard and Granados (1967) for unmodified wood and by Spalt (1958) and Papadopoulos and Hill (2003) for acetylated wood. The W value for Belmadur wood (463.7) was remarkably higher than the W value for untreated wood (270.3) 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 were 0.72 and 0.75 for untreated and Belmadur wood respectively, 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.

Applicability of the H-H model

Adsorption isotherms are shown in Figure 1. Equilibrium moisture content of Belmadur wood was reduced at all relative humidities compared to the untreated wood, 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. The isotherms for monomolecular and polymolecular adsorption are plotted in Figures 2 and 3, indicating a reduction in the hygroscopicity of wood at both monomolecular and polymolecular level.

Table 4, presents the reduction in the hygroscopicity at saturation. It can be seen that Belmadur wood was shown lower total sorption by 26.5%, polymolecular sorption by 23.9% and monomolecular sorption by 33.1% at saturation, compared with the untreated wood.

Mechanisms of reduction

The relation between total sorption and the ways in which it is held within the cell walls at saturation was verified by regression analysis of the EMC values at saturation for Belmadur wood. The results of this analysis which are presented in the upper part of Table 5, show clearly that the variation in total water sorbed is dependent on both monomolecular and polymolecular sorption. However, the higher F-ratios and R^2 values shown by the relationship between polymolecular and total sorption indicate that the variation shown in the water sorbed at the polymolecular level plays the main role in the variation in total water sorbed. This observation is in line with that made by Martins (1992) in wood modified with monofunctional isocyanates, and by Papadopoulou and Hill (2003) in wood modified with linear chain carboxylic acid anhydrides.

It is of interest at this point to assess how the decrease in site accessibility and the increasing volume of adducts in the cell wall (an expression of the degree of bulking) affect both total, monomolecular and polymolecular sorption. In the Hailwood-Horrobin model, W is the molecular weight of the sorptive substance associated with one mole of water in hydrate form at saturation. Accordingly, sorption site accessibility decreases with increasing W values. The higher W value of Belmadur wood (463.7, see Table 3) indicate that the availability of bonding sites is progressively reduced, resulting in decreasing monomolecular sorption. This is because the proportion of sorption sites also increases and therefore less free hydroxyl sites are left available for hydrogen bonding to water molecules. Additionally both polymolecular and total sorption are reduced. The presence of the adducts not only reduces monomolecular sorption by decreasing site

accessibility as discussed above, but also causes a great degree of bulking in the wood cell wall. Therefore, the reduction in site accessibility is accompanied by cell wall bulking. Thus, regression analysis of the of the EMC values at saturation was carried out in order to assess the effect of decreasing site accessibility (expressed as W) in the cell wall upon the total, polymolecular and monomolecular sorption.

The results of the analysis, which are presented in the lower part of Table 5, show that the decrease in site accessibility is dependent on both monomolecular, polymolecular and total sorption. However, better correlation for W is found when this factor is related to monomolecular sorption. This is indicated by the higher F-ratios and R^2 values in all relationships considered. It seems therefore, that only the reduction in monomolecular sorption can be primarily attributed to the decrease in site accessibility.

Conclusions

In this study, the water vapour sorption of Belmadur wood is fully investigated. The sorption isotherms were analysed using the Hailwood-Horrobin model. Belmadur wood was shown lower total sorption by 26.5%, polymolecular sorption by 23.9% and monomolecular sorption by 33.1% at saturation, compared with the untreated wood. Regression analysis of the EMC values at saturation revealed that the variation shown in the water sorbed at the polymolecular level plays the main role in the variation in total water sorbed. In addition, it was found that only the reduction in monomolecular sorption can be primarily attributed to the decrease in site accessibility.

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TABLE 1 SATURATED SALT SOLUTIONS USED AND THEIR RESULTANT RELATIVE HUMIDITIES AT 20 °C

Salt	RH (%)
Potassium nitrate (KNO ₃)	93
Sodium chloride (NaCl)	76
Sodium dichromate (Na ₂ Cr ₂ O ₇)	55
Potassium carbonate (K ₂ CO ₃)	44
Potassium acetate (CH ₃ COOK)	23
Lithium chloride (LiCl)	12

TABLE 2 MEAN VALUES FOR EXPERIMENTALLY DERIVED EMC'S AT VARIOUS LEVELS OF RH FOR THE UNTREATED AND BELMADUR WOOD. (STANDARD DEVIATION IN PARENTHESES)

Wood	EMC (%)					
	12	23	44	55	76	93
Untreated	2.33 (.05)	4.19 (.09)	7.02 (.02)	8.38 (.09)	12.68 (.1)	18.95 (.2)
Belmadur	1.45 (.04)	2.36 (.08)	4.29 (.08)	5.11 (.1)	7.85 (.09)	12.01 (.1)

TABLE 3 FITTED AND PHYSICAL CONSTANTS CALCULATED FOR THE HAILWOOD-HORROBIN ADSORPTION ISOTHERMS

Wood	A	B	C	K ₁	K ₂	W	R ²
Untreated	4.03	9.17	8.78	4.13	0.72	270.3	0.95
Belmadur	6.72	15.64	15.59	4.09	0.75	463.7	0.96

TABLE 4 REDUCTION IN THE HYGROSCOPICITY (%) AT SATURATION OF BELMADUR WOOD

Wood	Reduction in Hygroscopicity (%)		
	Total	Polymolecular	Monomolecular
Treated	34.7	32.8	41.3

TABLE 5 REGRESSION ANALYSIS RESULTS OF THE RELATION BETWEEN TYPES OF SORPTION AND TOTAL SORPTION AT SATURATION

Relation Examined	Belmadur Wood	
	F-ratio ¹	R ²
Monomolecular vs Total	37.44	90.3
Polymolecular vs Total	312.86	98.7
W ₀ vs Monomolecular	50.7	92.7
W ₀ vs Polymolecular	8.91*	69
W ₀ vs Total	13.94*	77.7

¹Significant at 95 percent level of probability. All the other values are significant at 99 percent level of probability.

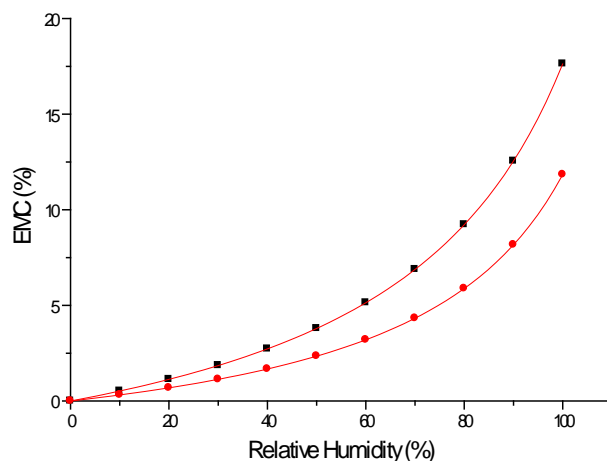


FIGURE 2 POLYMOLECULAR ADSORPTION ISOTHERMS FOR UNTREATED (■) AND BELMADUR (●) WOOD

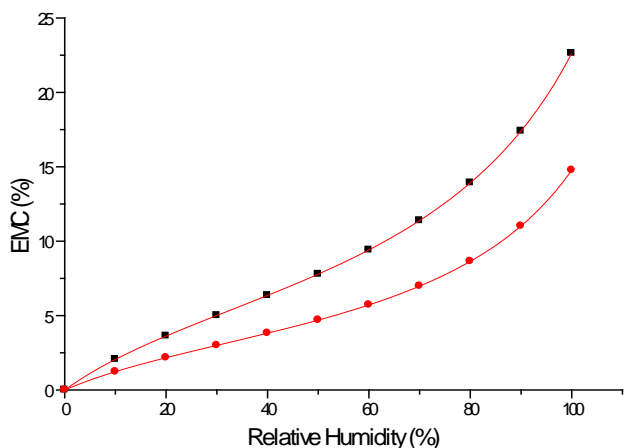


FIGURE 1 ADSORPTION ISOTHERMS FOR UNTREATED (■) AND BELMADUR (●) WOOD

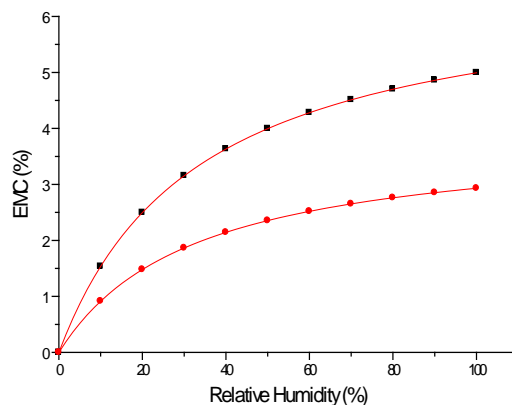


FIGURE 3 MONOMOLECULAR ADSORPTION ISOTHERMS FOR UNTREATED (■) AND BELMADUR (●) WOOD