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The sorption of water vapour of wood treated with a nanotechnology compound

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Abstract The potential of improving the hygroscopicity of solid wood by applying a new nanotechnology compound was investigated. The sorption isotherms were analysed using the Hailwood–Horrobin model. The experimental analysis of the sorption isotherms showed that the treatment affected total, polymolecular and monomolecular sorption. The application of the compound reduced the total sorption by 26.5%, polymolecular sorption by 23.9% and monomolecular sorption by 33.1% at saturation.

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; Hager and Mayer 1994). Wood may also be modified chemically or thermally so that selected properties are enhanced in a more or less permanent fashion (Rowell 1983; Hill 2006).

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An option to improve the hygroscopicity of solid wood is to exploit the solutions that nanotechnology can offer. Employing nanotechnology on wood can result in a next generation of products having hyper-performance and superior service ability when used in severe environments, since it is well known that the cell wall of wood exhibits porosity of molecular scale dimensions due to the partial filling of space between the cellulose microfibrils by lignin, hemicelluloses and extractives (Wegner et al. 2005; Wegner and Jones 2006). The small size nanoparticles of such nanotechnology compounds can deeply penetrate into the wood, effectively alter its surface chemistry and result in high protection against moisture. The aim of this research work therefore was to investigate the sorption of water vapour of wood treated with a new nanotechnology compound.

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

Description of the nanotechnology compound

A new nanotechnology compound, namely SurfaPore^{TM} W, was supplied by the company NanoPhos SA and selected in order to investigate the potential of improving the sorption of water vapour of wood. SurfaPore^{TM} W is a water based formulation designed to harness the power of nanotechnology in order to preserve absorptive wooden surfaces. The formulation consists of three different nanoparticle sizes, specially designed to penetrate into the mass of wood. The finest nanoparticles are intended to penetrate through the capillaries and bond with the hydroxyl groups of the cellulose content. The larger nanoparticles are intended to penetrate at the appropriate depth and react with the wood polymers. Finally, the formulation is completed by a nano-emulsion of paraffin that is intended to endure surface protection. The physical and chemical properties of SurfaPore^{TM} W are shown in Table 1.

Application of the nanotechnology compound

Sapwood samples of dimension 20 mm × 20 mm × 5 mm (radial × tangential × longitudinal) were cut from freshly felled kiln dried Corsican pine and carefully smoothed with sandpaper to remove loosely adhering fibres. After

Table 1 Physical and chemical properties of the SurfaPore™ W

Colour	Milky white
pH	8.8
Boiling and flash point	>100°C
Auto ignition point	>100°C
Density	0.98 g/cm^3
Viscosity	20 mPa s
VOC content	38 g/l (EU limit 130 g/l)
Solid content	14.32% w/v

conditioning at 20°C and 65% relative humidity for a week, the samples were immersed in a bath containing 1 l of the compound for 30 s at room temperature. The 30-s immersion in the compound caused negligible swelling. Subsequently, the samples were wiped off excess of the chemical and re-conditioned as described earlier. The uptake of the SurfaPore™ W solution was 140 g/m^2 of the sample surface. Samples were then oven dried at 105°C for 8 h and their weight was recorded.

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 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, constant RH is maintained (Siau 1984).

Six salts were chosen, and they are listed in Table 2 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). EMC was reached within 3 weeks for all but the two highest RHs, which required longer exposure times.

Table 2 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 ($Na_2Cr_2O_7$)	55
Potassium carbonate (K_2CO_3)	44
Potassium acetate (CH_3COOK)	23
Lithium chloride (LiCl)	12

Results and discussion

Isotherm fitting

The mean (average values obtained from two replicate samples) moisture contents at each RH of various modified woods are given in Table 3. 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

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

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

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

$h(\%)$ 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:

$$M = M_\mathrm{h} + M_\mathrm{d} = \frac{1{,}800}{W}\left(\frac{K_1K_2h}{100+K_1K_2h}\right) + \frac{1{,}800}{W}\left(\frac{K_2h}{100-K_2h}\right) \tag{5}$$

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 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:

Table 3 Mean values for experimentally derived EMCs at various levels of RH for untreated and treated Corsican pine samples

Wood	EMC (%)					
	12	23	44	55	76	93
Untreated	2.6 (0.1)	4.6 (0.1)	7.8 (0.1)	9.0 (0.2)	13.8 (0.1)	20.5 (0.4)
Treated	1.9 (0.1)	3.2 (0.0)	5.3 (0.1)	6.4 (0.0)	9.5 (0.2)	15.4 (0.1)

Standard deviation in parentheses

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

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

$$W = 1{,}800\left(\frac{4AC + B^2 + B\sqrt{B^2 + 4AC}}{B + \sqrt{B^2 + 4AC}}\right) \tag{8}$$

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 4. 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 indicate 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) and Wangaard and Granados (1967) for unmodified wood and by Spalt (1958) and Papadopoulos and Hill (2003) for acetylated wood. The W value for treated wood (397.9) was remarkably higher than the W value for untreated wood (250.3) indicating that a proportion of sites are made unavailable for water sorption.

As defined earlier, 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 0.77 for untreated and treated 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.

Table 4 Fitted and physical constants calculated for the Hailwood–Horrobin adsorption isotherms

Wood	A	B	C	K_1	K_2	W	R^2
Untreated	3.51	8.81	8.25	4.45	0.72	250.3	0.94
Treated	4.44	15.25	14.43	5.44	0.77	397.9	0.97

Applicability of the H–H model

Adsorption isotherms are shown in Fig. 1. Equilibrium moisture content of treated 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 Figs. 2 and 3, indicating a reduction in the hygroscopicity of wood at both monomolecular and polymolecular level.

Table 5 presents the reduction in the hygroscopicity at saturation. It can be seen that the application of the compound was to reduce total sorption by 26.5%,

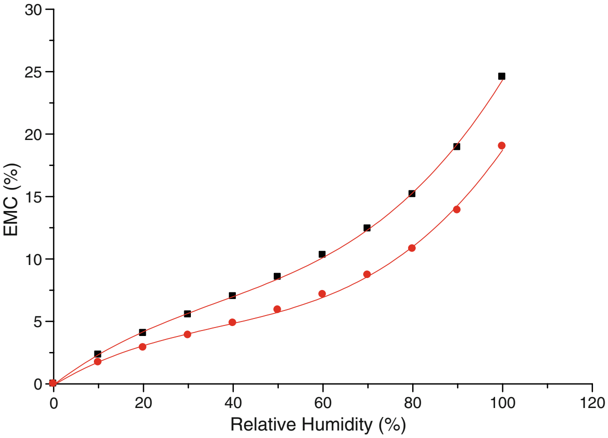

Fig. 1 Adsorption isotherms for untreated (*filled square*) and treated (*filled circle*) wood

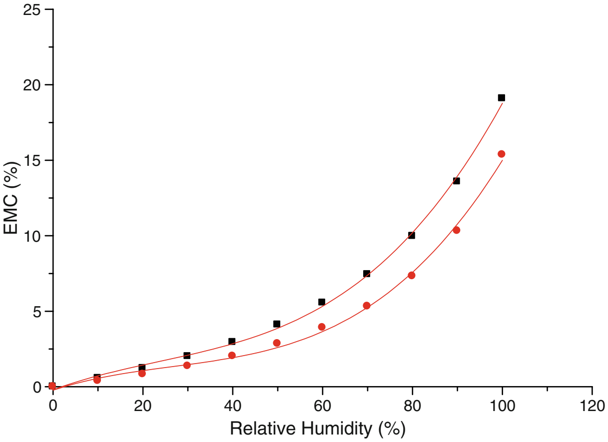

Fig. 2 Polymolecular adsorption isotherms for untreated (*filled square*) and treated (*filled circle*) wood

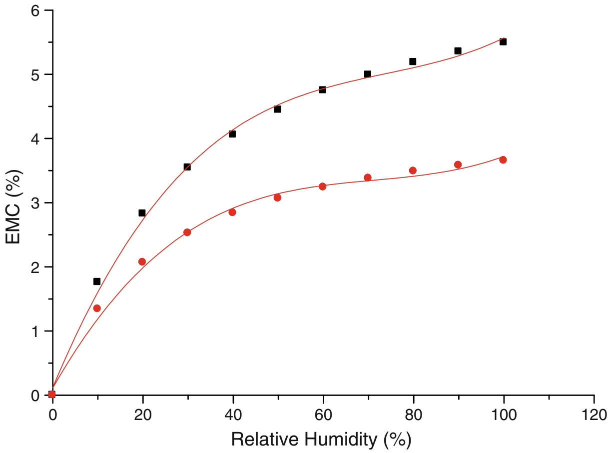

Fig. 3 Monomolecular adsorption isotherms for untreated (*filled square*) and treated (*filled circle*) wood

Table 5 Reduction in the hygroscopicity (%) at saturation as a result of the treatment with the compound

Wood	Reduction in hygroscopicity (%)		
	Total	Polymolecular	Monomolecular
Treated	26.5	23.9	33.1

polymolecular sorption by 23.9% and monomolecular sorption by 33.1% at saturation.

It was impossible to find available comparable data in the literature on the use of similar compounds for improving the hygroscopicity of solid wood. A recent study, however, on wood based panels showed that the application of the compound SurfaPore^{TM} W resulted in a significant improvement in the thickness swelling of the panels tested (Mantanis and Papadopoulos 2009). Therefore, it can be concluded that nanotechnology compounds may be an option to reduce the hygroscopicity of solid wood. SurfaPore^{TM} W is an aqueous wood-water repellent and easy to apply without changing the surface appearance. It does not contain any preservatives or other hazardous solvents and can be applied as a primer before the application of varnish or any other coating. Future work should focus on the investigation of the leachability of such compounds from wood in moist conditions and on the durability of the nanotechnology treatments after accelerated weathering.

Conclusion

The potential of improving the hygroscopicity of solid wood by applying the aqueous wood-water repellent SurfaPore^{TM} W was investigated. The sorption isotherms were analysed using the Hailwood–Horrobin model. The experimental analysis of the sorption isotherms showed that the treatment affected both total, polymolecular and monomolecular sorption. The application of the compound reduced the total sorption by 26.5%, polymolecular sorption by 23.9% and monomolecular sorption by 33.1%, at saturation. It can be concluded that nanotechnology compounds may be an option to reduce the hygroscopicity of solid wood.

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