

Water Vapor Sorption Kinetics of Wood Modified with Glutaraldehyde

Yanjun Xie,¹ Callum A. S. Hill,¹ Zefang Xiao,² Zaihan Jalaludin,¹ Holger Militz,² Carsten Mai²

¹Centre for Timber Engineering, School of Engineering and the Built Environment, Edinburgh Napier University, Edinburgh EH10 5DT, United Kingdom

²Wood Biology and Wood Products, Burckhardt-Institute, Georg August University of Göttingen, Göttingen D37077, Germany

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ABSTRACT: The modifying effects of Scots pine (*Pinus sylvestris* L.) wood with the crosslinking agent glutaraldehyde (GA) on the water vapor sorption kinetics were studied by curve fitting the experimental isotherm sorption data obtained using a Dynamic Vapor Sorption apparatus using the parallel exponential kinetics model (PEK model) and the Hailwood–Horrobin model (H–H model) for the isotherm. Both the H–H model and the PEK model provided good fits to the experimental data. Modification of wood with GA reduced both the time to equilibrium and the equilibrium moisture content (EMC). According to the PEK and H–H models, the reduction in EMC was mainly due to the decrease of moisture content (MC) associated

with the slow sorption processes and polylayer water. The fast sorption processes and monolayer water were little affected by GA modification. Compared to the untreated control, the estimated total water absorbed by wood treated to a WPG of 20.9% at 100% RH decreased by 52.2%, by extrapolating the fitted curves derived from the H–H model. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1674–1682, 2010

Key words: wood cell wall crosslinking; glutaraldehyde; bulking; water vapor sorption kinetics; parallel exponential kinetics (PEK) model; Hailwood–Horrobin (H–H) model

INTRODUCTION

Wood is a hygroscopic material because the cell walls contain abundant water sorption sites (hydroxyl groups). Most of the wood properties concerning utilization, such as dimensional instability and fungal decay, are closely related to the wood's water sorption behavior.¹ The interaction of water with cellulosic materials involves a dynamic proton exchange on the cellulose internal pore surfaces.^{2–4} The water sorption behavior of cellulosic and lignocellulosic materials is complex due to the complex internal geometry of the cell wall and also the continuous structural change resulting from cell wall dimensional variation.

Chemical modification is one of the approaches used to change the moisture sorption properties of wood primarily through the covalent bonding of chemicals with the hydroxyl groups of the cell wall polymers or by depositing sterically fixed compounds, mainly of high molecular weight, in the cell wall microvoids.⁵ Glutaraldehyde (GA) (pentane-1,5-

dial) is a dialdehyde that can in principle react with four hydroxyl groups of the cell wall polymers and may, therefore, be used as a cross-linking agent to modify wood. An aldehyde functionality can react with one hydroxyl group to form a hemiacetal and, subsequently, with a second to form an acetal. The former group is susceptible to hydrolysis, whereas the latter is stable under both neutral and acid conditions. The crosslinking reaction can be facilitated by heating the treated wood in the presence of catalysts.^{6–8} Treatments of Scots pine sapwood with GA and magnesium chloride as a catalyst to a weight percent gain (WPG) of 21% has been shown to result in a reduction of the EMC up to 30% at 90% RH compared to an untreated control. The antiswelling efficiency at water saturation can reach as high as 70% when wood is treated to a WPG of ~20%.⁶ GA treatment reduces both maximum swelling and shrinking, suggesting that both bulking and crosslinking occur within the wood cell walls.

Determining the EMC of wood at a given relative humidity (RH) is a means of evaluating the sorption properties of wood and the effectiveness of wood modification.⁵ The gravimetric method is a suitable way to determine the EMC by conditioning the wood samples over different saturated salt solutions at constant temperature to attain a desired RH.^{9,10}

Correspondence to: Y. Xie (y.xie@napier.ac.uk).

Recently, dynamic vapor sorption (DVS) has been used to investigate the sorption properties of different natural fibers,¹¹ cotton fabric,¹² and Sitka spruce wood.¹³ This DVS technique, yields highly reproducible data, is able to provide accurate isotherms over a wide RH range and the isotherm temperature can also be varied.¹¹ In the context of this article, the ability to gather "real time" data allows for the analysis of sorption kinetics behavior.

Utilizing this technique, the dynamic water vapor sorption properties of Scots pine (*Pinus sylvestris* L.) wood samples modified with GA have recently been studied, revealing considerable reduction in EMC over the hygroscopic range due to GA treatment.¹⁴ Modification with GA primarily reduced the sorption rates in the high RH range. The sorption hysteresis exhibited between adsorption and desorption isotherms was considerably reduced, and the desorption isotherm curves displayed quasi-linear behavior in this RH range for GA-modified samples.

Although sorption isotherm studies of wood are plentiful, relatively little attention has been given to the sorption kinetics process. In the past, this absence in the literature was due to the difficulty of making accurate measurements during the sorption process. The relatively recent introduction of DVS apparatus by a number of manufacturers allows for the ready determination of such properties.

Previous attempts to model sorption kinetic processes have utilized Fick's law on the assumption that the rate limiting step is a diffusion process, which is likely to be true for large wood samples. But in studies of cell wall sorption processes, where smaller particles are used, the kinetics may not be diffusion limited and indeed it has been shown unequivocally that the sorption kinetics fits a so-called parallel exponential kinetics (PEK) model for both plant fibers, wood and foodstuffs.^{11,15}

The main objective of this study was to establish the effect of GA modification on the sorption kinetics of wood by fitting the moisture content data obtained from the DVS apparatus. The sorption kinetics was evaluated using a PEK model and the Hailwood-Horrobin model (H-H model).

EXPERIMENTAL

Wood and chemicals

Wood blocks measuring 5 mm (longitudinally) × 20 mm (tangentially) × 20 mm (radially) were cut from the sapwood of Scots pine (*Pinus sylvestris* L.) boards. The modifying agent was a 50 wt % solution of glutaraldehyde (GA) supplied by BASF AG (Ludwigshafen, Germany). Magnesium chloride hexahydrate ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) was used as catalyst.

TABLE I
Chemical Compositions Used for Wood Treatment and Weight Percent Gain of Wood Obtained Accordingly

Treatment	Chemicals		Weight percent gain (%)
	Glutaraldehyde concentration (%)	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ concentration (%)	
I (control)	–	–	–
II	4	0.5	0.5
III	12	1.5	8.6
IV	20	2.5	15.5
V	30	3.75	20.9

Treatment of wood

Ten wood blocks were impregnated in aqueous acetate buffer solutions (0.1M, pH 4.5) of 4% (0.5%), 12% (1.5%), 20% (2.5%), and 30% (3.75%) GA (magnesium chloride hexahydrate), respectively, under vacuum conditions (100 mbar, 30 min) and pressure (10 bar, 1 h). The chemicals and their composition used for wood treatment were shown in TABLE I. After impregnation, excess treatment solution was blotted off the wood blocks with tissue paper, and the wood blocks were air dried for one week. Subsequently, the specimens were precured at 80°C (6 h) and then finally cured at 120°C (48 h).

After conditioning (20°C, 65% RH) for 24 h, all the untreated and treated specimens were leached with daily changed tap water for 1 week to remove the unreacted GA and magnesium chloride and subsequently oven dried at 103°C for 24 h and weighed. The treated and leached samples ultimately attained the weight percent gains of 0.5, 8.6, 15.5, and 20.9%, respectively. Untreated wood blocks served as control specimens. The untreated and treated wood blocks were ground into wood flour and passed through a 20 mesh sieve.

Determination of dynamic water vapor sorption

Isotherm analysis of wood flour was studied using a DVS Intrinsic apparatus (DVS, Surface Measurement Systems, London, United Kingdom) as previously reported.¹¹ Wood flour prepared as described earlier (ca. 20 mg) was placed on the sample holder, which is connected to a microbalance by a hanging wire, and is located in a thermostatically controlled cabinet. The preset RH was increased in steps in the following preprogrammed sequence (0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90, and 95% RH), before decreasing to 0% RH in the reverse order. The sorption processes were run at a constant temperature of 25°C over the full RH range. The instrument maintained a constant target RH until the sample moisture content change (dm/dt) was less than 0.002% per minute over a 10 min period. In practice, this

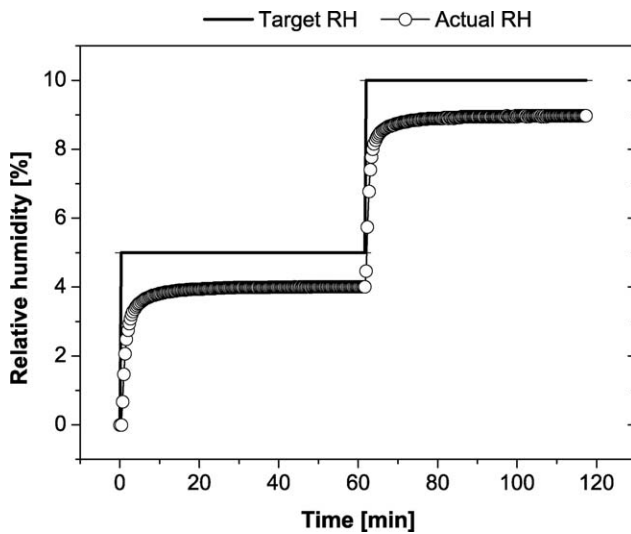


Figure 1 Typical changes of target relative humidity and actual relative humidity in the sample chamber during sorption process (The target relative humidity changed from 0 to 5% and subsequently 5 to 10%. Wood sample in the testing chamber was the untreated control).

does not mean that a true equilibrium is reached, but previous studies have established that this allows for obtaining EMC values within 0.1% of the true equilibrium value (i.e., at infinite time). The running time, target RH, actual RH, sample weight were recorded throughout the isotherm run.

Calculation of moisture content

The EMC of untreated and treated wood as measured by the DVS apparatus was calculated based on

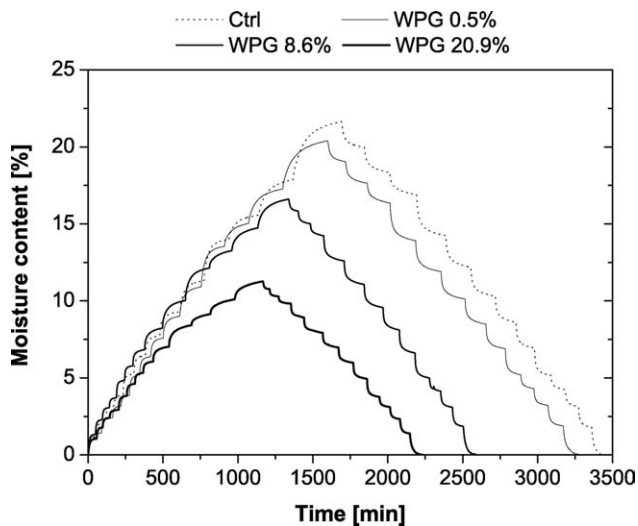


Figure 2 Kinetics of moisture content for wood untreated and treated to different WPGs with glutaraldehyde over time profile of isotherm during isotherm run in the full RH range.

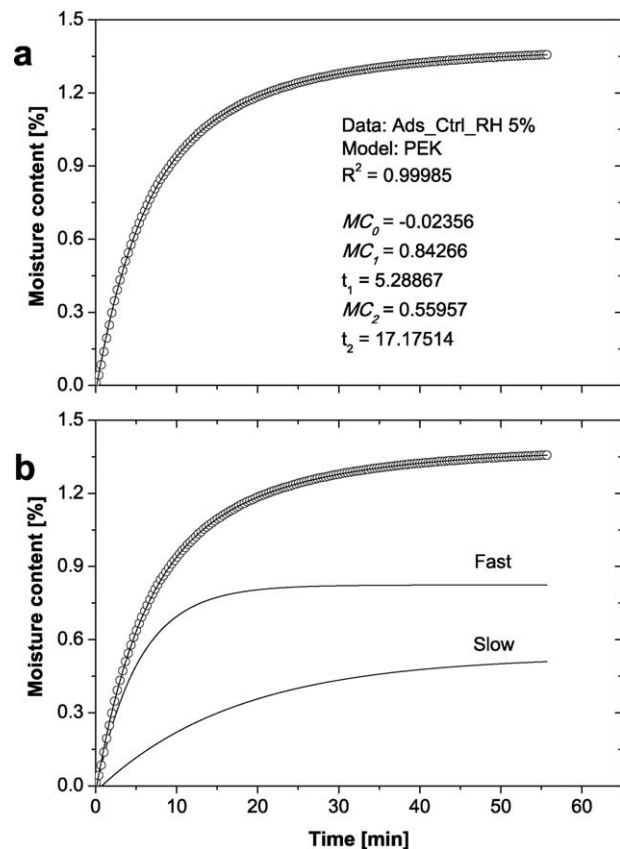


Figure 3 Example of PEK fit to experimental adsorption data (open circles) of untreated wood at 5% target relative humidity (a) and the fitted curves (lines) showing the slow and fast parallel exponential kinetic processes (b).

the mass of modified wood (referred to as MC) and on the mass of the same wood before modification (referred to as MC_R), respectively:

$$MC = \frac{m_2 - m_1}{m_1} \times 100 \quad (1)$$

$$MC_R = \frac{m_2 - m_1}{m_0} \times 100 \quad (2)$$

Where MC represents the measured moisture content of untreated and modified wood; MC_R represents the reduced moisture content of modified wood based on the mass of wood before treatment; m_0 is the dry weight of wood before modification; m_1 is the dry weight of wood after modification; m_2 is the equilibrium weight of wood at a given RH. MC takes no account of the fact that the mass of the sample is increased due to modification. MC_R , however, reflects the effect of incorporation of chemicals on the sorption isotherms of wood cell walls. For the untreated wood, m_0 equals m_1 and, thus, MC equals MC_R . In this context, all EMC values refer to the measured EMC (MC) unless otherwise stated.

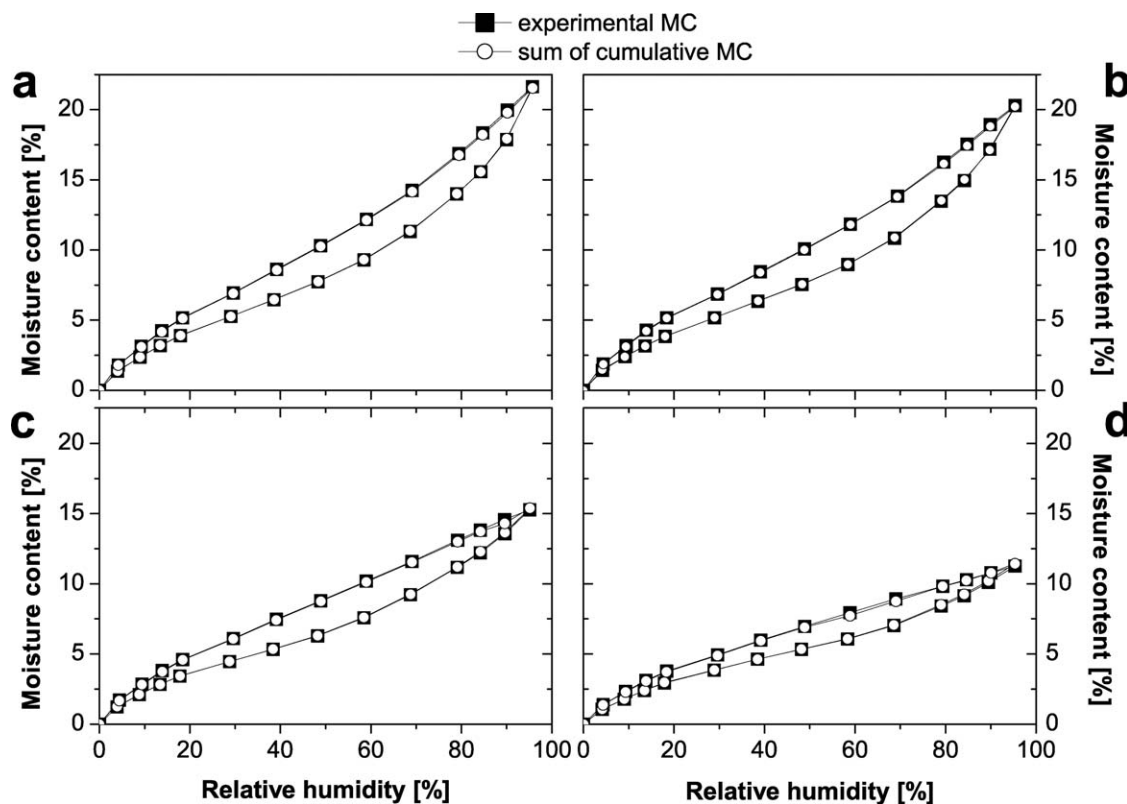


Figure 4 Comparison of sorption isotherm loops derived from experimental data and derived from sums of MC_0 , MC_1 , and MC_2 obtained from curve fitting using PEK model for wood untreated (a), or treated with glutaraldehyde to WPGs of 0.5 (b), 8.6 (c), and 20.9% (d), respectively.

RESULTS AND DISCUSSION

Sorption behavior of wood

The RH in the sample chamber did not immediately reach the target RH when the testing program changed the target RH from one value to the next during a sorption run (Fig. 1). This resulted in a transition time which can last for a few minutes. In most cases, the actual RH (at equilibrium state) was slightly lower than the target RH. The response of a wood sample to the changed actual RH produced an asymptotic curve approaching the EMC after infinite time of exposure at a given RH (Fig. 2). The moisture content of the wood gradually increased or decreased as a new target RH started until the sorption process reached the defined sorption state, and then the RH changed to the next preset RH (Fig. 2). Treatments with GA caused a reduction in EMC, which apparently decreased with the increase of WPG of wood. Compared to the EMC (21.6%) of untreated wood, wood treated to WPGs of 0.5, 8.6, 15.5, and 20.9% obtained EMCs of 20.3, 15.3, 12.4, and 11.26%, respectively, displaying considerably reduction in moisture adsorption of wood resulting from GA treatment. The total run time was also reduced by the GA treatments (Fig. 2).

Analysis using PEK model

A PEK model has previously been reported to provide exceptionally good fits to both adsorption and desorption curves for regenerated cellulosic lyocell fibers,¹⁶ natural fibers,¹⁵ and wood.¹³ In this study, the experimental data acquired at each target RH were curve-fitted using Origin 6.1 software (Origin-Lab Corporation, USA) to the function "expassoc" which has a double exponential form:

$$MC = MC_0 + MC_1(1 - e^{-t/t_1}) + MC_2(1 - e^{-t/t_2}) \quad (3)$$

where MC is the moisture content at infinite time of exposure of the sample to a constant RH, MC_0 is the moisture content of the sample at time zero. The sorption kinetic curve is composed of two exponential terms which represent a fast [$MC_1(1 - e^{-t/t_1})$] and a slow [$MC_2(1 - e^{-t/t_2})$] process having characteristic times of t_1 and t_2 , respectively. The terms MC_1 and MC_2 are the moisture contents at infinite time associated with the fast and slow processes, respectively.

An example for a kinetic curve fit of the experimental data using the PEK model is presented in Figure 3(a), which showed an excellent fit to the experimental data of untreated and treated wood in

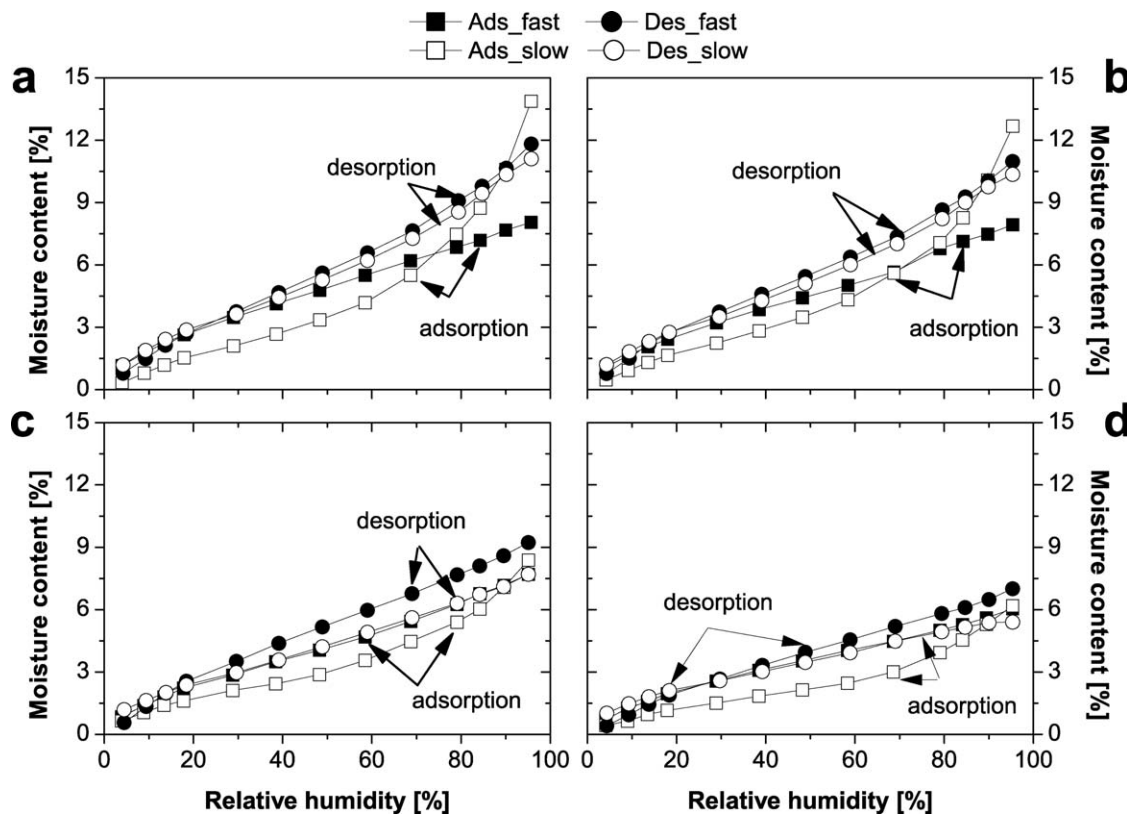


Figure 5 Cumulative moisture content associated with the fast (MC_1) and slow (MC_2) exponential kinetic processes in the water vapor adsorption and desorption run for wood samples untreated (a), or treated with glutaraldehyde to WPGs of 0.5 (b), 8.6 (c), and 20.9% (d), respectively.

this study ($R^2 > 0.99$). Typically, the fitted curve can be deconvoluted into a fast process associated with moisture content (MC_1) and a slow process associated with moisture content (MC_2) at infinite time t according to eq. 3 [Fig. 3(b)]. The fast kinetic process has been proposed to be related to the fast moisture sorption at the sites of “external” surfaces and “amorphous” regions, whereas the slow kinetic process has been related to sorption onto the “inner” surfaces and “crystallites.”^{16,17} The slow process has been described as a rate limiting step associated with the cell wall swelling process.¹³ However, it is not yet known what these two processes represent in terms of physical processes taking place within the cell wall. The sorption isotherm obtained from the PEK fitting was created by summing the cumulative moisture contents associated with the fast and slow kinetic processes and the moisture content at time zero ($MC_0 + MC_1 + MC_2$) in the adsorption and desorption runs. This fitted isotherm was comparable to the experimental isotherm loop for wood untreated and treated to different WPGs [Fig. 4(a–d)], indicating that the EMC values as measured by the instrument are very close to those predicted by the model at infinite exposure time.

The cumulative fast and slow processes for each subsequent RH step in the adsorption and desorp-

tion isotherm are shown in Figure 5. The untreated wood had more mass gain associated with the fast process than the slow process in the adsorption region below 70% RH after which the slow adsorption process began to dominate [Fig. 5(a)]. At the highest RH of 95%, the untreated wood displayed a MC associated with the fast process of 8.0% and 13.9% with the slow process. Modification with GA reduced the sum of cumulative MC with an increase of WPG (Fig. 5); however, the modified wood had generally similar fast and slow adsorption process characteristics to that of the untreated sample [Fig. 5(b–d)]. The MC associated with both the fast and slow adsorption in the high RH range of 80–95% decreased as WPG increased; and the decrease was greater in the slow process than in the fast process (Fig. 5(b–d)). As a result, the fast process became increasingly dominant in the full RH range with an increase of WPG. According to the previous assumption that the fast process represents adsorption onto readily accessible OH sites, whereas the slow process is associated with gradual diffusion to less accessible sites within the cell wall,¹³ the decreased domination of the slow process in this study may be explained by the fact that the crosslinking modification by GA makes wood more stiff with less resultant swelling,⁶ which may

TABLE II
Weight Percent Gain and Parameters of Hailwood–Horrobin Model A , B , C , K_1 , K_2 , and W Calculated Based on Measured Moisture Content (MC)

Treatment	WPG (%)	A	B	$C \times 10^3$	K_1	K_2	W
Ctrl	0	2.585	0.134	1.2	7.632	0.780	313.235
4% GA	0.5	2.543	0.140	1.2	8.294	0.754	320.872
12% GA	8.6	2.719	0.167	1.4	9.227	0.747	373.901
20% GA	15.5	3.005	0.176	1.3	9.827	0.663	388.577
30% GA	20.9	3.249	0.190	1.4	9.826	0.662	419.281

reduce the ability of water in the cell wall to open up new sorption sites.

In the desorption process, the cumulative MC of both fast and slow processes decreased with increasing WPG (Fig. 5). There was minor distinct difference found between fast and slow processes for the untreated samples or those treated to a low WPG (0.5%) [Fig. 5(a,b)], and at higher WPG levels, such difference increased, showing a higher MC associated with fast desorption process than that associated with slow process in the high RH region [Fig. 5(c,d)].

The moisture contents associated with the fast kinetic processes were similar between the adsorption and desorption cycles in low RH range; however, with the increase of RH the moisture contents exhibited hysteresis (Fig. 5). Chemical modification of

wood with GA distinctly reduced the hysteresis [Fig. 5(b–d)] compared to the untreated wood [Fig. 5(a)]. For the moisture contents associated with the slow processes, the hysteresis was primarily exhibited in the RH range up to 90%. Increasing the WPG due to the modification also resulted in a distinct reduction in the MC associated with the slow processes in both the adsorption and desorption runs. As a result, the degree of hysteresis remained similar to that of the untreated control.

Analysis using the Hailwood–Horrobin model

The adsorption behavior of wood at each RH was analyzed by fitting the experimental data using the Hailwood–Horrobin model (H–H model) as previously reported:¹¹

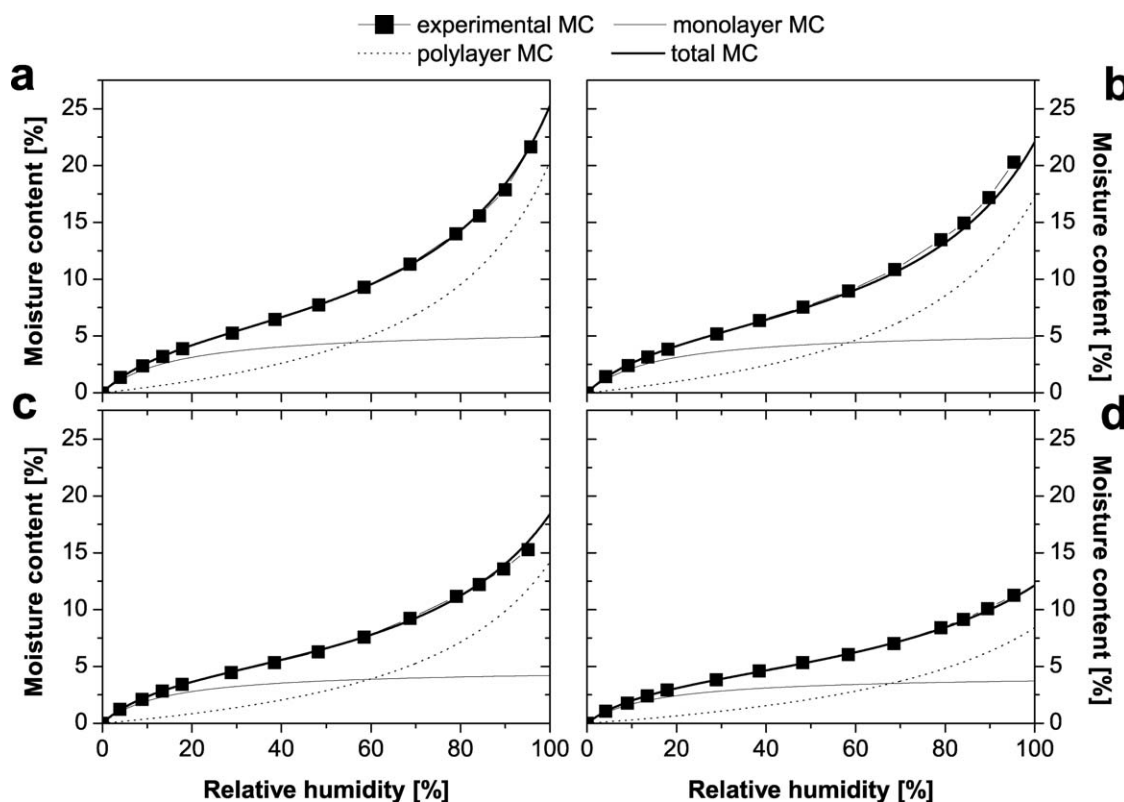


Figure 6 Monolayer, polylayer calculated using the Hailwood–Horrobin model, and the sum of monolayer and polylayer (total) adsorption isotherm through the relative humidity run compared to the experimental moisture content of wood untreated (a) or treated with glutaraldehyde to WPGs of 0.5 (b), 8.6 (c), and 20.9% (d), respectively.

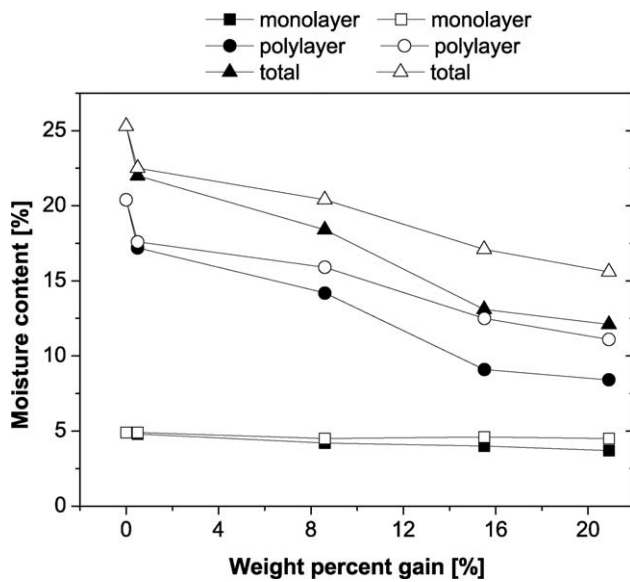


Figure 7 Comparison of monolayer, polylayer and estimated total water of untreated and treated wood at 100 RH attained by extrapolating the fitted curves to 100% RH level using the Hailwood–Horrobin model. The filled symbols showed the data calculated from the moisture content based on the mass of modified wood (MC) and the open symbols showed data calculated from reduced moisture content (MC_R).

$$M = M_h + M_s = \frac{1800}{W} \left(\frac{K_1 K_2 H}{100 + K_1 K_2 H} \right) + \frac{1800}{W} \left(\frac{K_2 H}{100 - K_2 H} \right) \quad (4)$$

Where M is the EMC at a given relative humidity (H), M_h is the moisture content from monolayer sorption, M_s is the moisture content due to polylayer sorption,¹⁸ K_1 is the equilibrium constant of the monolayer water formed from dissolved water and cell walls, K_2 is the equilibrium constant between water vapor and dissolved water, and W is the molecular weight of cell wall polymer per mole of water sorption sites. To fit the experimental data, a polynomial equation is used:

$$\frac{H}{M} = A + BH - CH^2 \quad (5)$$

Where A , B , and C are regression coefficients including constant (K_1 and K_2) and W . These values can be calculated using the equations as follows:

$$A = \frac{W}{18} \left[\frac{1}{K_2(K_1 + 1)} \right] \quad (6)$$

$$B = \left(\frac{W}{1800} \right) \left[\frac{K_1 - 1}{K_1 + 1} \right] \quad (7)$$

$$C = \left(\frac{W}{180000} \right) \left[\frac{K_1 K_2}{K_1 + 1} \right] \quad (8)$$

$$K_1 = 1 + \frac{B^2 + \sqrt{B^2 + 4AC}}{2AC} \quad (9)$$

$$K_2 = \frac{50(-B + \sqrt{B^2 + 4AC})}{A} \quad (10)$$

$$W = 1800\sqrt{B^2 + 4AC} \quad (11)$$

The detailed theory of the H–H model has been previously described.^{19–21}

The changes of WPG of treated wood affected the fitting parameters of A , B , C , K_1 and K_2 , while fitting to the experimental MC data (Table II). The constant K_2 decreased with increasing WPG, indicating a reduced activity of dissolved water in the microcapillaries.²⁰ The molecular weight of dry wood polymer per mole of water sorption sites (W) increased up to 34% at the highest WPG level of 20.9% compared to the untreated wood, which could be explained by blocking of some wood hydroxyl sites due to crosslinking reaction with GA. Other chemical modifications such as 1,3-dimethylol-4,5-dihydroxyethyleneurea (DMDHEU) and acetylation have also been reported to have an increased W with the WPG.^{8,22,23} The increase of the W value can be interpreted as the reduction in the number of free hydroxyl groups resulting from the chemical crosslinking between GA and cell wall polymers. However, Papadopoulos and Hill⁹ also found that W decreased in proportion to WPG when wood was modified with anhydrides of different molecular weight, showing that W is not related to OH content, but rather cell wall bulking.

The fitted curve using the H–H model coincided well with the experimental adsorption isotherm of untreated wood [Fig. 6(a)]. The monolayer water deconvoluted from the fitted sigmoidal isotherm increased rapidly at RH values below 20% and the increase afterward was lower. In the low RH range, the polylayer adsorption was lower than the monolayer adsorption, implying that the monolayer adsorption dominates the adsorption isotherm at the initial stage. The polylayer adsorption became dominant above the RH of ca. 55% [Fig. 6(a)]. The total moisture content above 70% RH was slightly underestimated in the case of wood treated to a low WPG of 0.5% [Fig. 6(b)]. At the WPG level of 8.6%, the total moisture content was, however, overestimated above 85% RH [Fig. 6(c)]. Both total MC and experimental EMC coincided very well for the wood

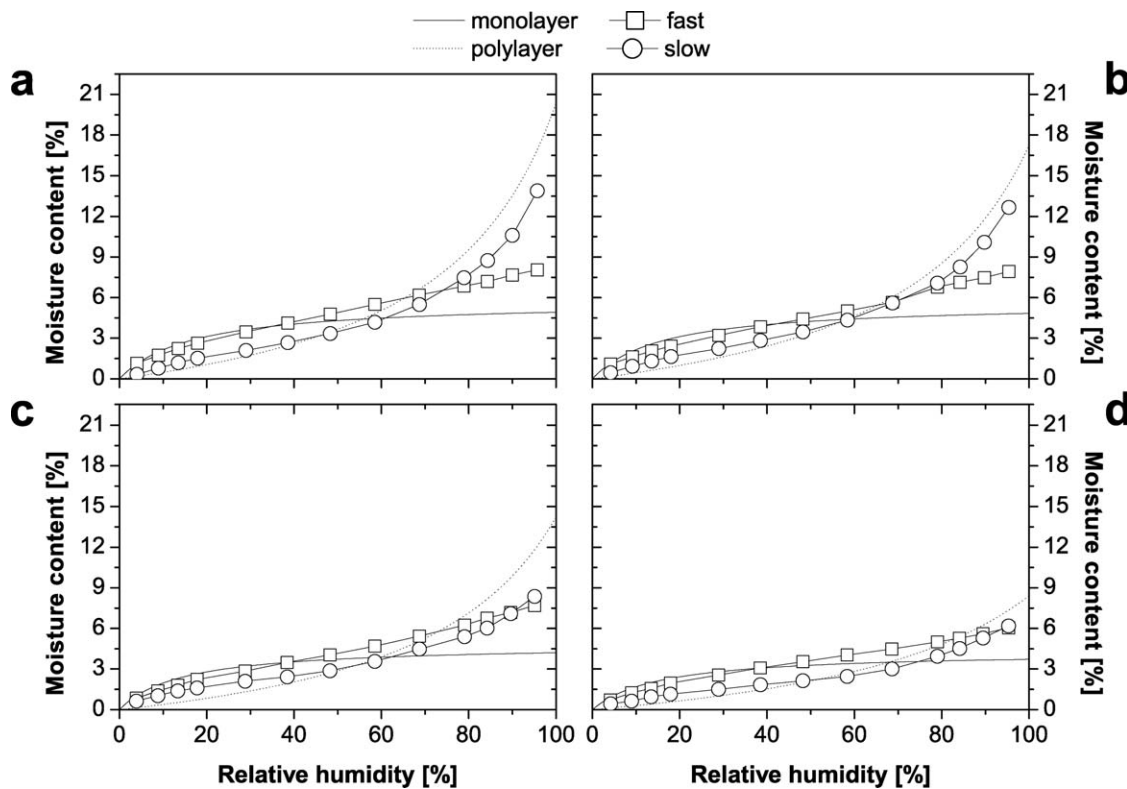


Figure 8 Comparison of cumulative moisture content values associated with the fast (MC_1) and slow (MC_2) exponential kinetic processes with the monolayer and multilayer moisture contents derived from the H–H model fit during adsorption process of wood untreated (a), or treated glutaraldehyde to WPG of 0.5 (b), 8.6 (c), and 20.9% (d), respectively.

sample treated to a WPG of 20.9% [Fig. 6(d)]. The monolayer water of wood was slightly influenced by the modification with GA during the adsorption isotherm run. This was somewhat different from the anhydride treated wood where it was found that the monolayer apparently decreased with the WPG at a projected 100% RH level.^{23,24} The decrease of EMC due to GA modification with the increased WPG is mainly attributed to the reduction of polylayer water adsorption [Fig. 6(b–d)]. This may be interpreted by the reduced nanopore size due to filling of GA and by the restrained swelling due to crosslinking of cell walls.^{6,25}

At a RH of 100% attained by extrapolating the fitted curve, the monolayer water adsorption exhibited a minor reduction with the increase of WPG (Fig. 7). Modification of wood with GA caused a distinct reduction of the polylayer water adsorption, especially when modified to a high WPG (Fig. 7). The untreated wood in this study displayed an estimated total MC of 25.3% which is somewhat lower than the fiber saturation points commonly reported for European softwood species (28–32%).²⁶ However, it is very well known that such extrapolation methods should not be used to determine the “true” fiber saturation point.²⁴ Treatment of wood to a WPG of 20.9% resulted in a reduction by 52.2% in the estimated total water ($M_h + M_s$) compared to untreated

control. At a similar WPG level, the estimated total water of GA-modified wood was comparable to that of wood modified with linear chain carboxylic acid anhydrides.²⁴ To determine the modifying effect, the reduced EMCs (MC_R) of modified wood were also calculated from which the estimated total water at RH 100% was attained using the H–H model. These estimated total water exhibited similar trends to but somewhat higher values than those derived from the measured moisture content (MC) (Fig. 7), indicating the reduction in the moisture content per unit cell wall mass. As it has been noted, GA has a smaller molecular weight and on a molar mass basis may deactivate more hydroxyl groups (via crosslinking) than the anhydrides (via grafting). At the similar WPG level, the GA-modified wood should have lower estimated total water because of more –OH deactivation than this of acetylated wood, which does not, however, apparently correspond to the experimental results. Consequently, the findings in this study support the previous point of view that estimated total water adsorbed by chemically modified wood at 100% RH is not determined by the extent of hydroxyl substitution of the cell wall, but is related to weight percent gain attained.²⁴

Comparing the monolayer and polylayer processes derived from H–H model to the fast and slow processes derived from PEK model, the monolayer

component exhibited an approximation to the MC of fast sorption process, whereas the polylayer water showed behavior associated with the MC of the slow sorption process (Fig. 8). The correlation is not good however, and on this basis assignments cannot be made between monolayer and polylayer water and the two kinetic sorption processes.

CONCLUSIONS

Modification of Scots pine sapwood with GA to different weight percent gains caused a reduction in the EMC. The kinetic model analysis reveals that the reduction in the EMC was mainly attributed to less moisture absorption in the slow process derived from the PEK model or in the polylayer water established from the H-H model. The MC of the fast process or the monolayer water adsorption was little influenced by GA treatment. The estimated total water of untreated and modified wood at 100% RH derived from H-H model is dominantly determined by weight percent gain (amount of incorporated chemical). The reduced EMC may therefore mainly be explained by the deposition of GA in the nanopores of wood cell walls resulting in the reduction of free pore space. Crosslinking between GA and cell walls may also deactivate the hygroscopic hydroxyl groups of cell walls and prevent the expansion of nanopores, thereby, making the cell wall stiffer. This study demonstrates that both models, the PEK model and the Hailwood-Horrobin model, can provide good fits to the experimental EMC, but further work needs to be done to pursue the interpretations of the PEK model and the potential correlations between the PEK and H-H models.

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