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The reduction in the fibre saturation point of wood due to chemical modification using anhydride reagents: A reappraisal

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Abstract

The data from a previous study of the moisture adsorption of Corsican pine modified with linear chain carboxylic acid anhydrides (acetic, propionic, butyric, valeric, hexanoic) has been reanalysed so that moisture content is reported as a percentage of cell wall mass only. As part of this work, the change in fibre saturation point (FSP, determined from fits of the Hailwood-Horrobin model) of the modified wood has been determined as a function of weight percentage gain (WPG). The change in FSP is not determined by the extent of hydroxyl substitution of the cell wall, but is related to WPG only (as reported previously). This is also true for the relationship between monolayer water, polylayer water, molecular weight per sorption site at saturation and WPG. However, there is no simple linear relationship between calculated FSP and WPG. When the FSP was determined by solute exclusion methods, the reduction thereof could be simply explained as due to bulking of the cell wall by the bonded acyl substituents. This is not the case when the FSP is determined from adsorption isotherms. This result is interpreted as an ambiguity of determination of FSP from projections of sorption isotherms. Differences in FSP determined by the two methods (sorption versus solute exclusion) are considered to be due to incomplete wetting of the lignocellulosic material when absorbing moisture from the initial dry state.

Keywords: acetylated wood; fibre saturation point; Hailwood-Horrobin model; sorption isotherm.

Introduction

Chemical modification of wood with acetic anhydride (and other linear chain anhydrides) results in changes to the physical and biological properties of the material. The majority of these property changes appear to be determined by the weight percentage gain (WPG) of the material rather than extent of hydroxyl substitution. These include dimensional stability (Stamm and Tarkow 1947; Hill and Jones 1996; Li et al. 2000), decay resistance (against *Coniophora puteana*) (Papadopoulos and Hill 2002a; Hill et al. 2005) and hygroscopicity reduction (Papadopoulos and Hill 2002b; Papadopoulos et al. 2005).

To determine whether bulking (i.e., the space occupied in the cell wall by the bonded substituents) is responsible for a change in any property, it is first necessary to determine the true volume that the substituent occupies within the cell wall. This is not normally possible to determine with any degree of certainty by techniques relying upon measurement of changes in external dimensions, and these methods are likely to result in flawed data (Hill and Ormondroyd 2004; Heon Kwon et al. 2007). However, helium pycnometry is well suited to determine cell wall bulking. Hill et al. (2005) were able to show that the reduction in fibre saturation point (FSP), as determined by solute exclusion, correlated with the degree of bulking of the cell wall due to the presence of covalently bonded acyl substituents.

Papadopoulos and Hill (2002b) demonstrate that the reduction of equilibrium moisture content (EMC) due to reaction of Corsican pine with a variety of anhydrides correlated with the WPG due to reaction irrespective of anhydride; however, the values of EMC reported were calculated on the basis of the mass of the anhydride modified wood (i.e., mass of wood substance plus mass of bonded reagent). Unfortunately, such an analysis can result in errors when conclusions are drawn regarding the mechanism of hygroscopicity reduction. This is because the reduction in EMC is a result of two processes. Firstly, the effective weight of the wood has increased due to the presence of reagent, thus there will be an apparent reduction in EMC in any case, even if the amount of water in the wood cell wall remains the same. Secondly, there may be a genuine reduction in EMC, because the bonded reagent bulks the cell wall or because hygroscopic OH groups are blocked (Hill 2006).

To understand the effect of wood modification upon the sorption-desorption properties of modified wood, the EMC values should therefore be based upon the oven-dry weight of the wood substance prior to modification, rather than the actual weight of the sample (i.e., weight of wood substance plus weight of adduct). This point has been noted previously and in some studies a reduced EMC (EMC_R) rather than measured moisture content is employed [Eq. (1)] (Akitsu et al. 1993).

$$EMC_R\ (\%) = [(M_2 - M_1)/M_0] \times 100 \qquad (1)$$

where M_0 is the oven-dry weight of the specimen before modification, M_1 is the oven-dry weight of the specimen after modification, and M_2 is the weight of the modified specimen at equilibrium with the atmosphere at a given relative humidity (RH).

In the work reported herein, the original data of Papadopoulos and Hill (2002b) has been used to calculate values of EMC_R, and the FSP has then been deduced from the Hailwood-Horrobin (H-H) fits to these data. The results thus obtained have been used to determine whether the reduction in FSP due to anhydride modification is due to a bulking phenomenon or to other effects.

The H-H model was originally developed to describe the adsorption isotherm of water onto cotton, which is a sigmoidal type II isotherm (Hailwood and Horrobin 1946) (Table 1). The first application of this model with acetylated wood was described by Spalt (1958) and this work was subsequently referred to by both Skaar (1972) and Siau (1984). Popper and Bariska (1972) reported H-H polylayer and monolayer isotherm data for acetylated fir. Yasuda et al. (1995) studied a range of modified woods and Chauhan et al. (2001) investigated esterified rubber wood sorption behaviour with the H-H model. Papadopoulos and Hill (2002b) investigated the sorption properties of Corsican pine modified with a range of anhydride reagents by the same approach. Papadopoulos et al. (2005) subsequently found that the (H-H) model gave the best fit to experimental data. However, none of these studies reported the data in terms of EMC_R.

The H-H model considers the state of equilibrium existing between a vapour phase, a liquid phase (in cell lumina) and a solid solution (in the cell wall). The classic sigmoidal shape of a sorption isotherm is deconvoluted by the H-H model into a monolayer (Mh) and a polylayer (Ms) component [Eq. (2)].

$$M = M_h + M_s = \frac{1800}{W}\left(\frac{K_1K_2H}{100+K_1K_2H}\right) + \frac{1800}{W}\left(\frac{K_2H}{100\text{-}K_2H}\right) \tag{2}$$

where M is the percentage moisture content at a given percentage relative humidity (H), W is the molecular weight of cell wall polymer per sorption site and K_1 and K_2 are constants.

The values of K_1 and K_2 are determined by plotting H/M against H, which is predicted by the H-H theory to give a parabolic relationship of the form shown in Eq. (3).

$$\frac{H}{M} = A + BH\text{-}CH^2 \tag{3}$$

where K_1, K_2, W, A, B and C are linked by the following relationships:

$$A = \frac{W}{18}\left[\frac{1}{K_2(K_1+1)}\right] \tag{4}$$

$$B = \left(\frac{W}{1800}\right)\left[\frac{K_1\text{-}1}{K_1+1}\right] \tag{5}$$

Table 1 Hailwood-Horrobin parameters for data obtained from Papadopoulos and Hill (2002b), but based upon reduced equilibrium moisture content (EMC_R).

Anhydride		*a*	*b*	*c*	K_1	K_2
Unmodified	0	3.44	0.106	0.00097	5.167	0.739
Acetic	5.2	3.90	0.119	0.00109	5.137	0.738
	11.4	4.24	0.134	0.00128	5.113	0.768
	15.8	4.66	0.165	0.00153	5.641	0.763
	19.6	6.42	0.149	0.00146	4.126	0.742
	22.5	8.55	0.128	0.00142	3.018	0.742
Propionic	5.3	4.24	0.115	0.00108	4.673	0.738
	11.2	4.90	0.136	0.00135	4.575	0.776
	15.3	5.39	0.162	0.00157	4.895	0.771
	20.1	6.97	0.157	0.00160	3.956	0.762
	25.7	9.18	0.133	0.00156	2.889	0.767
Butyric	5.5	4.52	0.115	0.00111	4.413	0.746
	11.1	5.51	0.110	0.00108	3.750	0.723
	16.0	5.90	0.156	0.00152	4.500	0.757
	20.1	6.82	0.147	0.00148	3.884	0.748
	26.1	10.14	0.135	0.00166	2.713	0.777
Valeric	4.9	3.95	0.115	0.00106	4.958	0.736
	10.9	4.75	0.147	0.00144	4.955	0.782
	15.5	5.42	0.134	0.00130	4.317	0.745
	19.8	6.12	0.187	0.00185	4.884	0.787
	26.2	9.45	0.158	0.00185	3.105	0.793
	28.9	8.42	0.119	0.00134	2.912	0.739
Hexanoic	5.7	4.72	0.105	0.00101	4.042	0.727
	12.1	5.16	0.123	0.00120	4.208	0.744
	15.7	5.39	0.143	0.00137	4.548	0.747
	19.5	7.10	0.161	0.00169	3.905	0.781
	25.4	8.07	0.162	0.00170	3.638	0.761
	29.1	7.74	0.161	0.00168	3.726	0.764

$$C=\left(\frac{W}{180{,}000}\right)\left[\frac{K_1K_2}{K_1+1}\right] \tag{6}$$

Note that Eq. (5) is given incorrectly by Yasuda et al. (1995). From the above relationships, the values K_1, K_2 and W can be derived as shown in Eqs. (7) to (9).

$$K_1=1+\frac{B^2+B\sqrt{B^2+4AC}}{2AC} \tag{7}$$

$$K_2=\frac{50\left(-B+\sqrt{B^2+4AC}\right)}{A} \tag{8}$$

$$W=1800\sqrt{B^2+4AC} \tag{9}$$

Note that Eq. (7) is given incorrectly by Papadopoulos and Hill (2002b).

The aims of this study were to determine the amount of absorbed moisture in anhydride modified wood on a cell wall mass basis (EMC_R) and to re-calculate new H-H fitting parameters from this modified data. To date no H-H fitting for modified wood has used EMC_R.

The absolute values of cell wall bulking (determined from helium pycnometry data) have been utilised to determine whether such bulking explains the reduction in FSP as the WPG increases. It has already been demonstrated that the level of OH substitution does not explain this reduction.

It is well known that FSP values determined from solute exclusion studies yield different values compared with sorption isotherm experiments. This study was designed to determine what the reason for this difference might be.

Experimental

The data of Papadopoulos and Hill (2002b) was the basis to generate isotherms based upon calculations of EMC_R. The values of monolayer and polylayer water at 100% RH were calculated by the H-H model and these were added together to calculate FSP. The helium pycnometry data of Hill and Ormondroyd (2004) and Heon Kwon et al. (2007) was used to determine cell wall volume occupied per mole of bonded acetyl group. Because these studies have not found a definitive molar volume for the acetyl group in acetylated Corsican pine, two values were used (30 cm^3 mol^{-1} and 40 cm^3 mol^{-1}), which represent the extreme range of molar volume values reported for this species. The reduction in FSP was then calculated on the basis that the cell wall volume occupied by the bonded acetyl group was unavailable to water molecules, as described by Hill et al. (2005). The assumption in this case is that the density of water in the cell wall is 1 g cm^{-3}.

Results and discussion

A plot showing the determinations of Mh and Ms water for an H-H fit to the sorption data of unmodified Corsican pine is presented in Figure 1. The summation of these yields the sigmoidal isotherm, which is compared with the best-fit polynomial through the data.

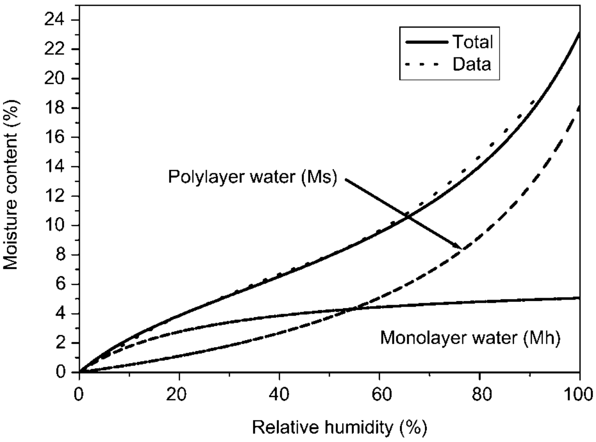

Figure 1 The variation in monolayer (Mh) and polylayer (Ms) water with relative humidity and a comparison of total moisture content (Mh+Ms) with experimental data for unmodified Corsican pine.

The values for cell wall moisture content at saturation as determined from solute exclusion (equivalent to EMC_R) and reported in Hill et al. (2005) are illustrated in Figure 2a. The straight lines on this plot have been generated assuming a molar volume of 30 or 40 cm^3 mol^{-1}, according to the method described by Hill et al. (2005). In generating these lines, a FSP of the unmodified wood is assumed to be 37.5%. Also shown is a least-squares

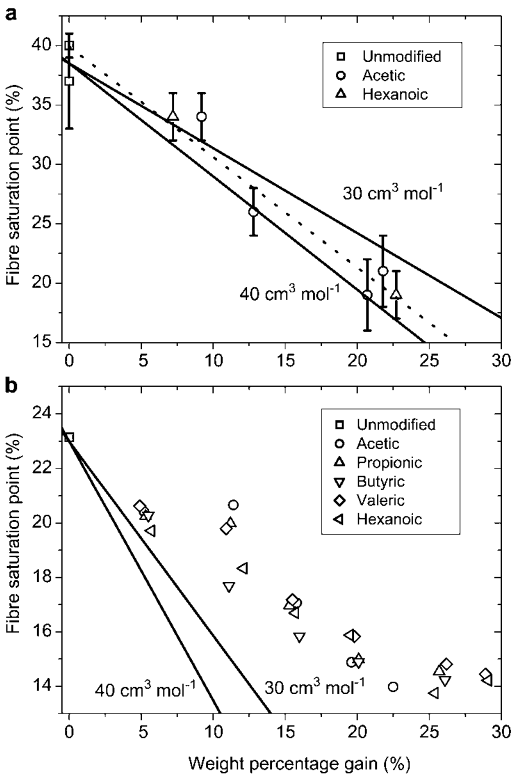

Figure 2 Plot showing the relationship between fibre saturation point (FSP) and weight percentage gain (WPG) for Corsican pine modified with a range of anhydrides. The linear fits are calculated based upon the molar volume occupied by acetyl groups, assuming a value of either 30 cm^3 mol^{-1} or 40 cm^3 mol^{-1} and assuming a fibre saturation point of modified wood of 37.5% for solute exclusion (a) and 23% for adsorption isotherm data (b). The dotted line is the least squares linear fit to the data points.

linear fit to the data points (dotted line). This falls within the region bounded by the two molar volume values for the most part, indeed if an FSP value of 40% is assumed, the best fit falls exactly on the line defined by a molar volume of 40 cm^3 mol^{-1}.

The values of the FSP for Corsican pine modified to different WPGs with a variety of anhydride reagents, as calculated from sorption EMC_R values, are presented in Figure 2b. This shows that although the FSP decreases as the WPG due to modification is increased, the relationship is clearly non-linear. The straight lines on this plot have been generated assuming the FSP of unmodified wood to be 23%, as determined from the H-H fits. This value is somewhat lower than those commonly reported for European softwood species (28–32%) according to Popper et al. (2006). If the reduction in FSP was solely due to bulking by anhydride reagent, then the experimental data points would fall on this straight line. In most cases, the data points are well clustered for all the anhydrides, suggesting that there is a common mechanism causing a reduction in FSP, and that this is not related to extent of hydroxyl substitution. It is obvious that the data points do not fall on the calculated line and two explanations can be forwarded to explain this. If the FSP obtained by extrapolating the isotherm data to 100% RH is correct, then the observed reduction is not due to cell wall bulking. Alternatively, it can be concluded that it is not possible to derive a 'true' FSP by extrapolating isotherm data. It is of interest to note that the EMC_R data above 25% WPG is close to what would be predicted from the solute exclusion results at this level of substitution.

The values for Mh and Ms water and molecular weight of polymer per sorption site (*W*) at saturation have been plotted against WPG and the results are shown in Figure 3. Linear fits (of the form $Y=A+B\times X$) to the data points have been performed and the fitting parameters are presented in Table 2. It should be noted that two data points (hexanoic and valeric anhydride at 29% WPG) were not included in the linear fits. The two points yield higher moisture content values than the general trend, which might be interpreted as being due to cell wall damage revealing new sorption sites at these high WPG values. In all cases, the linear fits are significant. However, the fit to the monolayer data yields a higher r-value than the multilayer data. No physical significance is attached to this difference, as the isotherms were generated from a relatively low number of data points, and errors can arise in fits where the polylayer water curve is rising rapidly. It is possible that the relationship between Ms and WPG is non-linear.

There is dispute as to whether FSP can be accurately determined using solute exclusion, as this invariably yields higher FSP values compared with many other techniques. Values for the FSP as determined by solute exclusion are found to be around 40%, which Siau (1984) attributed to the use of microtomed sections, resulting in there being less mechanical restraint of the cells. However, values of this order are also found for solid wood samples when the solute exclusion technique is applied (Hill et al. 2005). Alternatively, some workers have questioned the validity of using extrapolated isotherm data to

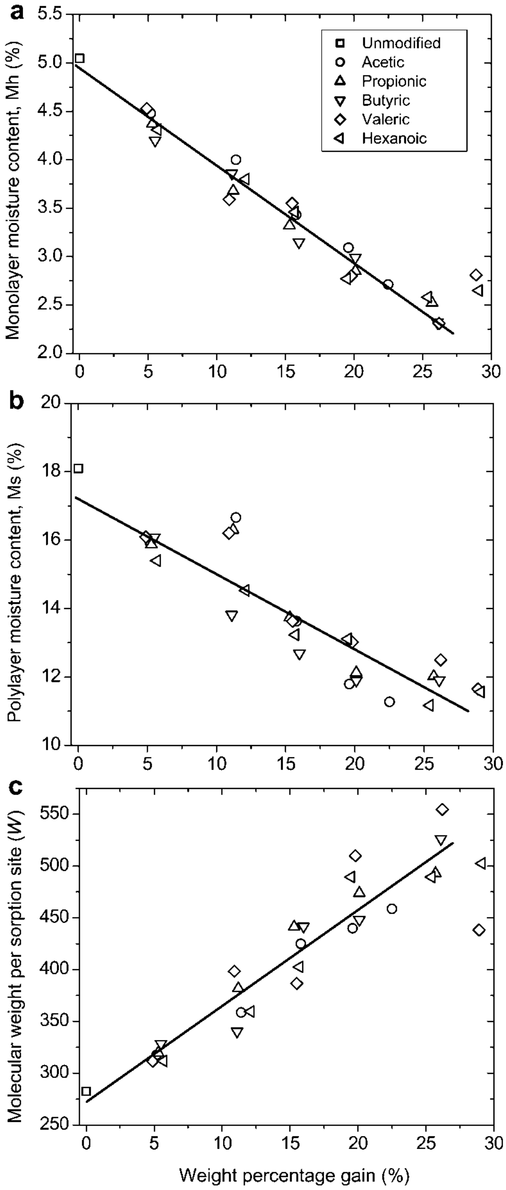

Figure 3 The variation in monolayer [Mh] (a) and polylayer [Ms] (b) water and molecular weight of polymer per sorption site [*W*] (c) with WPG for Corsican pine modified with a range of anhydrides (fitting parameters for linear fits are given in Table 2).

Table 2 Parameters for linear fits ($Y=A+B\times X$) of the data in Figure 3.

	A	*B*	Correlation coefficient	P-value
Monolayer water (Mh)	4.91	-0.0984	-0.985	<0.0001
Polylayer water (Ms)	17.47	-0.237	-0.910	<0.0001
Molecular weight per sorption site (*W*)	267.0	9.70	0.955	<0.0001

P is the value for the t-test of slope=0.

obtain FSP. There is some controversy regarding the absolute determination of FSP and there are differences in the value depending upon the determination methods.

It has been argued that the extrapolated sorption isotherms is untrustworthy, because in the region of 98–100%, the sorption isotherm is rising very rapidly and slight errors in measurement can lead to large errors in extrapolation. The isotherm in the range of 96–99% RH can only be determined by pressure plate methods (Hernández and Pontin 2006). Experiments based on isotopic exchange revealed that the FSP may be higher than 30% (Chow 1972). Ahlgren et al. (1972) investigated solute exclusion of a variety of wood substrates and reported some FSP values as high as 82%. Such high values are likely to be erroneous.

FSP was originally defined as the point at which the cell wall is saturated and all water absorbed after this point is in the lumen rather than the cell wall (Tiemann 1906). Whilst the definition is useful conceptually, it does not take into account the possibility that the situation occurring during sorption may be far more complex and there may be condensation in the lumen before the cell wall is saturated. Almeida and Hernández (2006a,b) and Hernández and Pontin (2006) studied the dimensional changes in wood as the EMC was reduced and concluded that there was loss of cell wall bound water above FSP. Babiak and Kúdela (1995) note that there are many different ways of measuring FSP and that the values, and in some cases the definitions of FSP, vary. They suggest instead a new term called the cell wall saturation limit y(CWS), defined as:

$$\mathrm{CWS}=(1/\rho_r-1/\rho_o)\rho_w\times 100 \tag{10}$$

where ρ_r is density of dry wood, ρ_w is the density of water and ρ_o is a value for the density of the water saturated wood calculated by the weight of the oven-dry wood divided by the volume of the water saturated wood.

However, the method is unfortunately flawed, because the volume of the water-saturated wood is calculated from external dimensions, which is not suited to determine the change of cell wall volume.

Stamm (1971) compiled different methods to determine FSP, noting that both solute exclusion and pressure plate methods yielded much higher values (both approximately 40% moisture content) compared to extrapolation of sorption isotherms. Stamm also reproduced a plot showing the sorption behaviour of basswood, which also includes the original desorption curve from the green state. On a subsequent adsorption cycle, the extrapolated FSP is reduced compared to the original value, a behaviour which is explained as being due to irrecoverable loss of sorption sites in the first drying cycle. However, the same behaviour is shown in the paper by Chen and Wangaard (1968) for a different species, but in this case, the desorption cycle from the wet state is for a sample of originally dry wood that was subsequently equilibrated over water.

Churaev et al. (1998) discussed the nature of water vapour sorption isotherms on porous surfaces where there is incomplete wetting of the substrate during the sorption process. This involves calculations of contact angles formed between the convex capillary menisci in narrow pores at RH values below saturation. In the case of incomplete wetting, the extrapolation of an adsorption isotherm to 100% RH will yield a value lower than that predicted if complete wetting occurs. Chen and Wangaard (1968) apply similar reasoning to the hysteresis observed in the sorption of water vapour by wood. The hysteresis effect is explained as being due to differences in the advancing and receding contact angle between wood and liquid water. Although these authors admit that invoking contact angles when studying vapour sorption can be criticised, they point out that at higher RH values (above 60%) capillary condensation is becoming dominant and that, as a consequence, the contact angle of a liquid on the pore surface can be considered with justification.

It is clear that extrapolation methods for determining FSP do not measure the same property as saturation methods (such as solute exclusion or pressure plate methods). It is therefore recommended that the term FSP is not used universally, and that the term ‘cell wall total water capacity’ is used for methods where true saturation of the cell wall is involved in the measurement process (Ibbett 2007), as is the case with solute exclusion studies.

Conclusions

This work has demonstrated that modification of wood with anhydride reagents results in a reduction in FSP, as determined by extrapolation of sorption isotherm data. However, the relationship between FSP and WPG is non-linear, indicating that the reduction in FSP is not due to a cell wall bulking phenomenon. These results are contrasted with the solute exclusion data, where it is shown that cell wall bulking by bonded acetyl is directly correlated with the reduction in the capacity of the cell wall to accommodate water molecules. It is clear that the two methods do not yield the same FSP and it is recommended that the term FSP is not used for methods where the wood is truly saturated compared to extrapolation methods.

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