The Water Vapour Sorption Properties of Anhydride Modified Wood

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ABSTRACT

This paper reports upon further analysis of previously reported water vapour sorption data for wood modified with different anhydride reagents. The data has been recalculated in terms of reduced equilibrium moisture content (EMC_R) and the reduction thereof as weight percentage gain of the wood increases is presented. The implications for the mechanism by which EMC_R decreases as a result of chemical modification are discussed in the light of this analysis.

INTRODUCTION

It is well known that chemical modification of wood results in a reduced capacity to absorb moisture when the wood is exposed to water vapour. Various explanations for this have been advanced related to the extent of hydroxyl (OH) substitution (hydrophobicity model) or the weight percentage gain (WPG) (bulking model) of the modified wood. By modifying wood with anhydride molecules of different molecular weight, Papadopoulos and Hill (2003) were able to demonstrate that the reduction in equilibrium moisture content (EMC) correlated with the WPG irrespective of the anhydride used for the modification, thereby confirming that bulking was the mechanism. Bulking is a measure of how much volume the bonded adduct occupies in the cell wall of the modified wood. This has been assumed to correlate with the volume change of the wood due to modification, but it was shown by Hill and Ormondroyd (2004) that this was not a safe assumption to make. This is because the volume change of the wood as determined by external dimension changes does not necessarily represent the change in volume at the cell wall level (measured using helium pycnometry). By the use of helium pycnometry, Hill and Ormondroyd (2004) were able to calculate the molar volume of the acetyl group in wood. This information was subsequently used by Hill *et al*. (2005) to determine what the theoretical cell wall water content of water saturated wood should be at different WPGs. This calculation was based upon the simple assumption that volume in the cell wall occupied by bonded acetyl was therefore not available for water molecules. Thus, it was shown that the reduction in cell wall water content measured using solute exclusion correlated with the volume denied due to presence of bonded adduct determined using helium pycnometry. Recently, Hill (2008) used the vapour sorption data of Papadopoulos and Hill (2003) combined with the helium pycnometry data of Hill and Ormondroyd (2004) and Heon Kwon *et al*. (2007) to determine the fibre saturation point (FSP) of anhydride modified softwood, using the 'reduced equilibrium moisture content' (EMC_R) of Akitsu *et al*. (1993). This showed that the reduction in FSP was linearly correlated with the WPG, showing that the reduction in cell wall moisture content was due to a bulking mechanism in the case of water vapour sorption. It was noted by Hill (2008) that using the projection of sorption isotherms to determine FSP is incorrect and that furthermore, it is highly unlikely that the classical definition of FSP has any meaning. What was not presented in that paper was any correlation of EMC_R at any other relative humidity values at different WPGs. This analysis is presented herein. Due to page limitations, no report is given of experimental techniques, but these have been fully described in the publications cited in this paper.

ANALYSIS OF RESULTS

The reduced equilibrium moisture content takes account of the fact that because of the presence of bonded adduct, the modified wood weighs more than unmodified and hence a calculation of the moisture content based upon the actual weight of the modified wood will automatically show a reduction. Instead, Akitsu *et al*. (1993) used a different parameter that they called the reduced equilibrium moisture content (EMC_R), which is calculated solely on the basis of the cell wall mass, as follows:

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

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 RH.

If any comparison is made of the effect of chemical modification upon wood with a view to understanding the mechanisms by which the vapour sorption properties are modified, it is necessary to use EMC_R, rather than EMC in order to remove the confounding effect of the increase of wood weight due to the presence of bonded adduct.

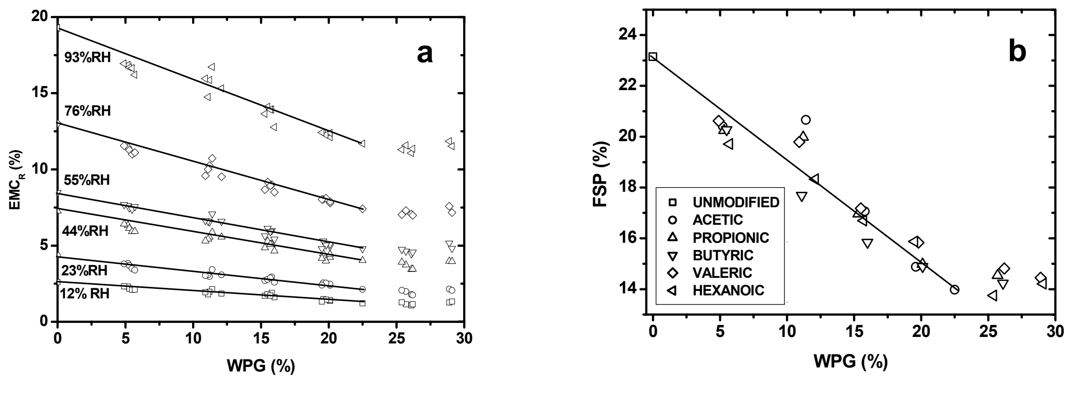

Figure 1: Variation of EMC_R with WPG at a given RH (a) and at FSP (b). In 1a the different anhydrides used for the modification are not delineated

The variation of EMC_R with WPG at different RH values is shown in Figure 1a above and the variation in 'FSP' with WPG is given in Figure 1b. These data are for Corsican pine modified with a series of linear chain anhydrides derived from the data reported by Papadopoulos and Hill (2003). For Figure 1a, the different anhydrides are not shown for reasons of clarity. Both graphs show that EMC_R or FSP decrease linearly as WPG increases, up to a WPG of 22.5%, but that the relationship is lost thereafter. This linear relationship indicates that bulking is the mechanism responsible for the reduction in cell wall moisture content as WPG increases. Helium pycnometry can be used to determine the volume occupied by the bonded acetyl group in the cell wall and from this it is possible to calculate a theoretical volume available to water in the cell wall, if it is assumed that the density of water in the cell wall is 1 gm cm^{-3}. Helium pycnometry of anhydride modified Corsican pine shows that the molar volume of the acetyl group in the cell wall is between 30-40 cm^3 per mole of adduct (Ormondroyd and Hill 2004, Heon Kwon *et al*. 2007). From this, it is simple to determine what the theoretical cell wall water content should be at different WPGs, as has been done by Hill *et al*. (2005) and the results compared with experimental data obtained by solute exclusion studies (Figure 2).

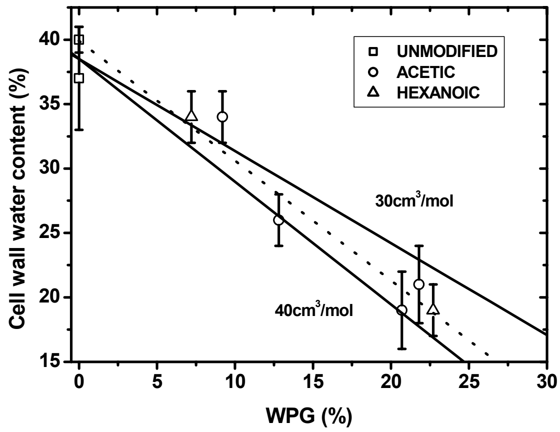

Figure 2: Change in cell wall water content at saturation as determined by solute exclusion. The two unbroken lines are theoretical water content calculated from helium pycnometry data. The broken line is the linear least squares fit to the solute exclusion data

There is an excellent correlation between the theoretical predictions and the experimental data, especially so if an acetyl molar volume of 40 cm^3 per mole is assumed. The question to be asked is does this also work when measuring the cell wall moisture content of wood or modified wood in equilibrium with the atmosphere at a given RH? This is shown in Figure 3 for modified wood at 12%RH, and 93%RH.

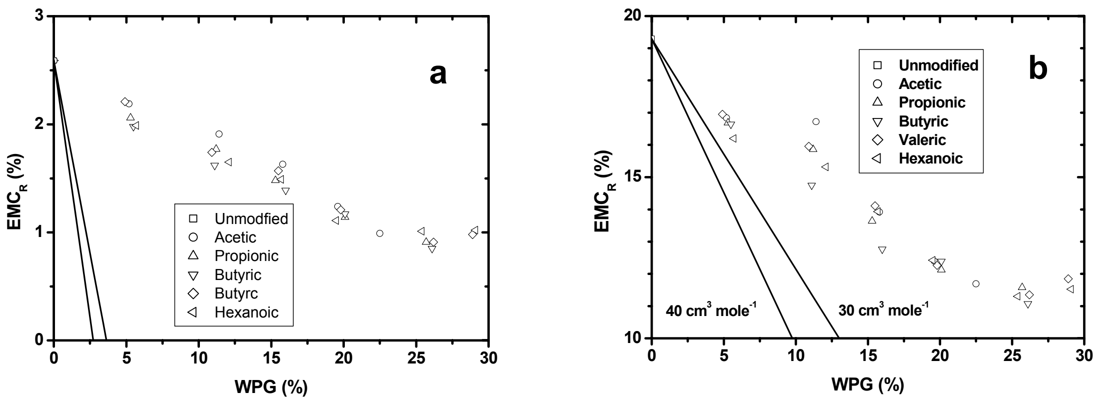

Figure 3: Plots showing the relationship between EMCR and WPG at 12%RH (a) and 93%RH (b), the lines show the theoretical cell wall moisture content based upon an acetyl molar volume of 30cm^3 per mole or 40 cm^3 per mole

These plots show that the closer the cell wall moisture content of the unmodified wood approaches the water saturated value of 40%, the better the fit between the theoretical lines and the data. What does this mean?

CONCLUSIONS

There is clearly a reduction in cell wall moisture content as WPG increases and this reduction is independent of the anhydride, hence cell wall bulking is the mechanism. However, when the theoretical reduction is calculated on the basis of the molar volume of the acetyl group, this only correlates with the data when the cell wall is fully water saturated.

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