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The role of hydroxyl groups in determining the sorption properties of modified wood

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ABSTRACT

In order to determine the influence that hydroxyl group content has upon the sorption isotherm, acacia (*Acacia mangium*) and sesendok (*Endospermum malaccense*) were thermally modified for different times and at different temperatures in order to achieve differing levels of thermal modification. In a separate experiment, birch samples were acetylated to different levels of weight percentage gain. The water vapour sorption isotherms of the thermally and chemically modified wood samples were determined using a dynamic vapour sorption (DVS) apparatus. Increasing temperature and increasing time of thermal modification, or increasing levels of acetylation both resulted in a reduction in the hygroscopicity of the samples. The hydroxyl group content was determined by using the deuterium exchange technique, also using a dynamic vapour sorption apparatus. With this method, the water reservoir in the DVS is filled with deuterium oxide rather than water. Although correlation was found between the reduction in hygroscopicity and OH content for acetylated birch, no clear relationship was found for the thermally modified wood samples.

INTRODUCTION

Acetylation and thermal modification can be applied to improve the properties of wood (Hill 2006). One consequence is the reduction in hydroxyl (OH) content within the cell wall, which reduces the number of primary sorption sites. Of the various potential chemical modifications, acetylation using acetic anhydride is the most studied and is also produced commercially. Acetylation reduces the EMC of the modified wood due to bulking and/or OH blocking. However, analysis of the sorption isotherm of acetylated wood requires caution. Chemical modification leads to an increase in the weight of the wood sample due to the addition of acetyl groups, which means that for a given mass of water in a given mass of wood substance, a lower EMC is measured due to the extra mass of the bonded acetyl groups. It is common practice to report the EMC of acetylated

wood, using the standard method of calculation (mass of water divided by mass of substrate). However, it is also essential to calculate a "reduced" EMC (labelled EMC_R), which takes account of the additional mass of the bonded acetyl and thereby reports the moisture content in terms of wood substance only. This allows for a better understanding of the mechanisms by which acetylation affects the sorption behaviour (bulking of the cell wall by bonded acetyl, or OH blocking, or a combination of the two). In a study intended to determine the mechanism by which acetylation reduces the moisture sorption of wood, Papadopoulos and Hill (2003) modified wood samples with a homologous series of linear chain anhydrides. In this way at comparable WPGs it was possible to have a range of levels of hydroxyl substitution. Subsequently, Hill (2008) re-evaluated this data in order to remove the effect of the weight of the bonded acyl groups, which can result in erroneous data. The conclusion from both these studies was that the reduction in EMC was due to bulking of the cell wall by the covalently bonded groups and that degree of hydroxyl substitution was not a factor. With these studies, the extent of OH substitution was calculated from the weight gain due to anhydride modification. It is also commonly believed that the reduction in hygroscopicity of thermally modified wood is due to a commensurate decrease in the accessible OH content of the wood, due to thermal degradation of the cell wall components. However, there has been not been any study where the level of accessible hydroxyl groups in modified wood has been directly measured and the research reported herein was conducted to make such a determination and furthermore to see if there might be any correlation between hydroxyl accessibility and EMC.

EXPERIMENTAL

The water sorption/desorption properties of chemically modified wood and the accessibility of the primary sorption sites evaluated by hydrogen-deuterium exchange can be determined by the dynamic vapour sorption technique in separate experiments. The DVS technique gives highly reproducible data and is able to supply precise sorption isotherms over a wide RH range. Analyses of the wood samples were performed using a dynamic vapour sorption apparatus (DVS Intrinsic, Surface Measurement Systems Ltd, London, United Kingdom). The wood samples were placed on the sample holder, which was connected to a microbalance by a hanging wire. This is located in a thermostatically controlled chamber through which there was a constant flow of dry nitrogen gas and into which was mixed another flow of nitrogen containing water vapour. For the deuterium exchange experiment, D_2O (99%) was used instead of water. The process uses a minimum of six sorption desorption cycles to ensure that full exchange of the accessible OH groups has occurred, as determined by a stable and positive mass gain due to exchange of the hydrogen atom by deuterium (Rautkari *et al*. 2013, Popescu *et al*. 2014). For determination of the sorption isotherms, the sorption/desorption RH was changed in steps of 5% RH from 0 to 95% RH and then again in reverse to 0% RH. The temperature was constant (25 ^{o}C) during the entire experiment. The instrument maintained the sample at a constant RH until the rate of mass change (dm/dt) was less than 0.002% per minute over a 10 min period. Data on mass change was acquired every 20 s. The running time, target RH, actual RH, sample weight were recorded throughout the isotherm run. Two tropical hardwood species, acacia (*Acacia mangium*) and sesendok (*Endospermum malaccense*), were selected for the study of thermally modified wood. The specimens were thermally modified in dry conditions at 180 °C, 200 °C and 220 °C for 1, 2, or 3 hours, prior to milling to fine particles (20 mesh). Full details of the sample preparation, thermal modification and measurements of the

sorption isotherms are presented by Jalaludin *et al*. (2010). Full experimental details of the acetylation of the birch samples are given in Popescu *et al*. (2014).

RESULTS AND DISCUSSION

A typical deuterium exchange experiment is shown in Figure 1. The DVS apparatus achieved a RH of 80-85% in the example illustrated, but it was enough to reach all accessible OH-groups, as evidenced by the stable mass change obtained in the dry masses of the later cycles. The accessibility was calculated from the difference between the initial dry weight of the sample and the dry weight after the sixth cycle, when the weight did not change anymore. It was found that the most significant weight change occurred in the first cycle and the difference can be seen in Figure 1.

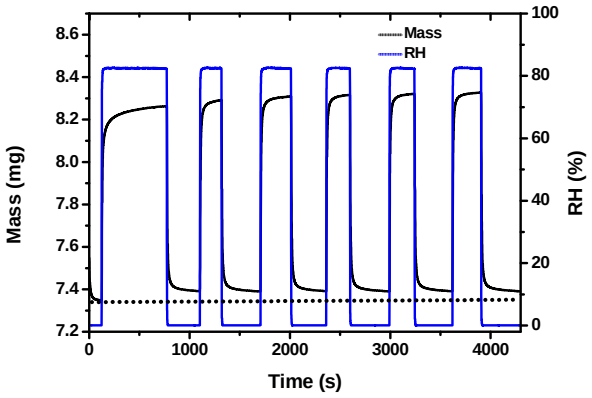

Figure 1: Example run for a deuterium exchange experiment

Changes in the sorption isotherm of thermally modified (220 °C, 3 h) and unmodified acacia wood are shown in Figure 2 and for birch with different levels of acetylation in Figure 3.

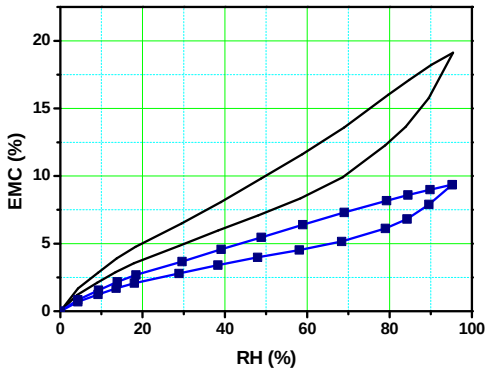

Figure 2: Reduction EMC as a result of thermal modification compared to unmodified wood

These both clearly show that there is a reduction in EMC as a result of modification of the wood. On close inspection it can also be observed that the desorption isotherm is more linear in character with the modified wood samples compared with the unmodified wood.

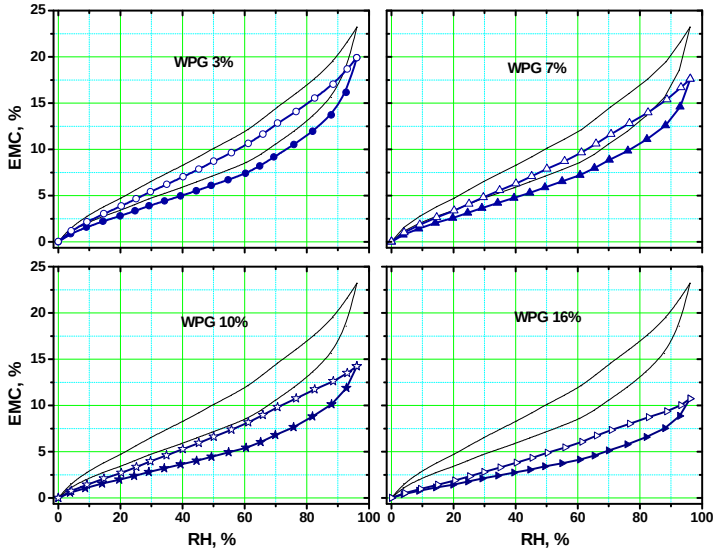

Figure 3: Changes in the sorption isotherm (EMC) with different levels of acetylation of birch, compared with unmodified birch isotherm

This is also observed when the reduced EMC (EMC_R) is plotted against RH (Figure 4).

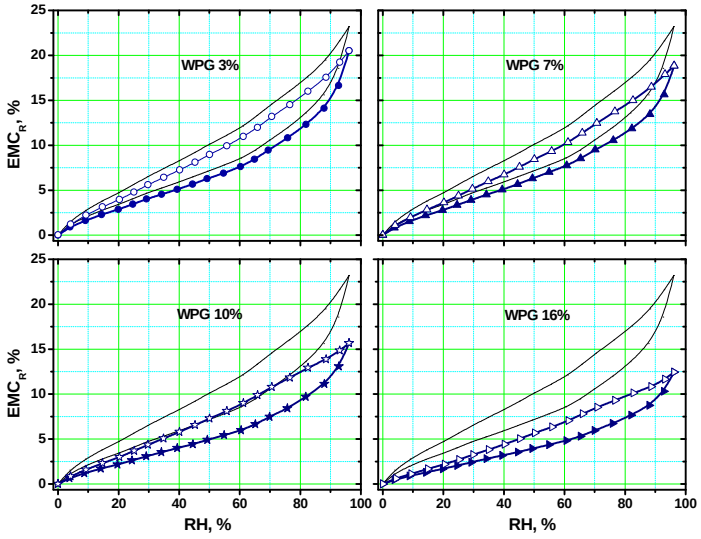

Figure 4: Changes in the sorption isotherm (EMC_R) with different levels of acetylation of birch, compared with unmodified birch isotherm

The accessible OH content, determined by the deuterium exchange experiments for the thermally modified acacia and sessendok is shown in Figure 5. The deuterium exchange experiments were run in triplicate and the standard deviations from these experiments are shown in the plots. Larger variations in the determined OH contents were found with samples modified for longer time periods with acacia. This is attributed to localised and random micro-cracking in the cell wall.

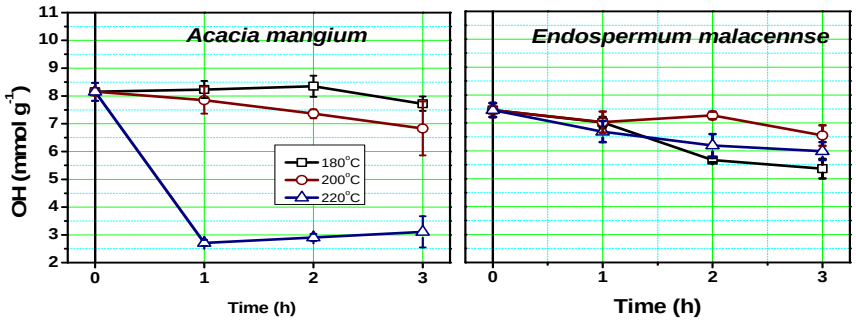

Figure 5: A comparison of the accessible OH content as determined using deuterium exchange for thermally modified acacia (LHS) and sessendok (RHS)

These plots show that there is a reduction in accessible OH content with increasing time and temperature of modification in most cases, but that the behaviour of the two species is different. With acacia, there is no reduction in accessible OH content at the lowest temperature of modification (180 ^{o}C), except for a modification period of three hours. At 200 ^{o}C there is a clear trend in the variation in accessible OH content and time of exposure. With the highest temperature of modification (220 ^{o}C) there is a dramatic reduction in OH content after modification for 1 hour, but no further reduction thereafter. This behaviour is anomalous and wholly unexplained. Although there is a reduction in OH content with time of thermal modification observed with sessendok, there is no correlation between the OH content and temperature of modification. Again, this behaviour is not what would be predicted and remains unexplained.

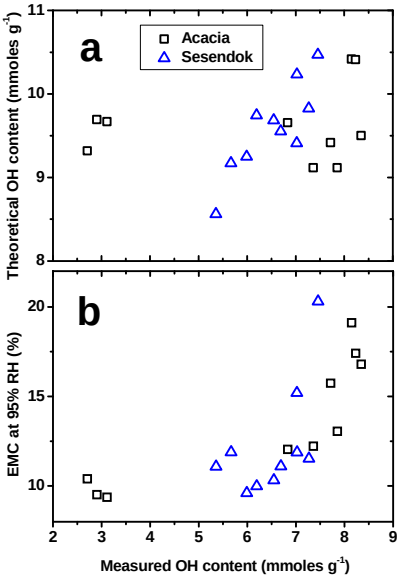

Figure 6: Relationship between theoretical and measured OH content (a) and between measured OH content and EMC at 95% RH for the thermally modified woods

The next step was to see if there was a correlation between the measured accessible OH content with the theoretical OH content calculated from the chemical composition (Figure 6a) and between measured OH content and reduction of EMC (measured at 95% RH) (Figure 6b). These two plots show that there is a very poor correlation between the

measured OH content and the calculated OH content obtained from the chemical composition using a standard calculation method (Rautkari *et al*. 2012). This is also the case where the EMC at 95% RH is plotted against the measured OH content. The latter observation is not what would be expected given the widely held scientific explanation that the OH groups are responsible for controlling the hygroscopicity of the wood. This would also apply to carboxylic groups, which may be present in higher concentration in thermally modified wood, but would nonetheless be detected in the deuterium exchange experiments.

This data at least requires a modification of the standard model, in order to incorporate some other factor influencing the hygroscopicity, such as the cell wall matrix modulus (Keating *et al*. 2012, Popescu *et al*. 2013). It is necessary to continue the work with thermal modification in order understand the surprising results that are presented in this paper. The wood used in these experiments was thermally modified by immersion in hot oil, which may have influenced the results, although the wood samples were taken from the interior of the specimens, where no penetration of the oil was observed. Further work needs to be done in order to examine the relationship between OH content and hygroscopicity of thermally modified wood.

When a similar analysis is performed for the acetylated birch (Figure 7), a good correlation is found between the measured OH content and the theoretical OH content (calculated from the WPG). However, there is an offset in the calculated OH content and the measured OH content, which is assumed to be due to the loss of some thermally labile material during the acetylation process.

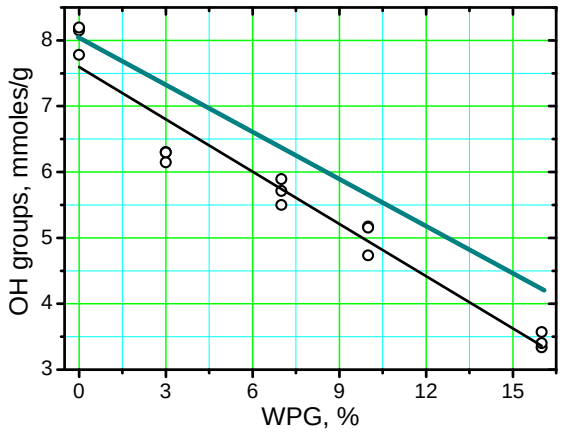

Figure 7: Relationship between accessible OH content and WPG, also showing the calculated OH content (upper line)

When the relationship between the EMC_R and OH content is examined, it is found that there is a very good correlation between these two properties (Figure 8). However, although the data appears to show that the OH content controls the EMC, it does not rule out some other mechanism, such as bulking, as is also shown in Figure 8, with the plot of WPG against EMC_R. Earlier work has already shown that the reduction in EMC_R is correlated with WPG rather than the accessible OH content, although this work relied upon calculation of Oh content rather than direct measurement (Hill 2008). Further work is currently underway using wood modified with different anhydrides to separate out the influence of OH content and bulking.

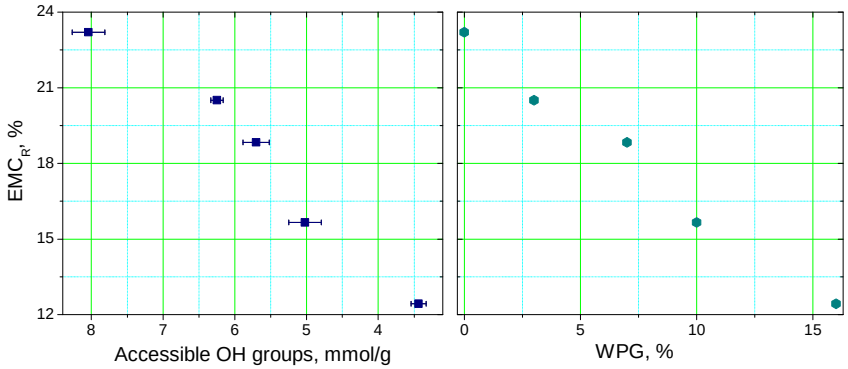

Figure 8: Showing relationship between EMC_R and the number of accessible OH groups (LHS) and between the number of OH groups and WPG (RHS)

CONCLUSIONS

Direct measurement of OH content of modified and unmodified wood has been undertaken using a newly developed DVS analytical method involving deuterium exchange. The relationship between accessible OH content and EMC has been examined. It has been found that with thermally modified wood there is a poor correlation between hygroscopicity and OH content, whereas with acetylated wood a good correlation has been found. This interesting method requires further development and research.

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