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ORIGINAL RESEARCH

Effect of acetylation on wood-water interactions studied by sorption calorimetry

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Abstract Sorption of water has a profound effect on the material properties of wood. The uptake of water vapour in wood and other materials releases more heat than the condensation of vapour to liquid water. This excess energy provides insights to the interactions and energy state of the absorbed water molecules. Modification of wood by acetylation is a common way of altering the wood-water interactions; however, very few data exist on how this and other types of modification affect the energy state of absorbed water in wood. This study is the first to use sorption calorimetry on modified wood to explore the effect of acetylation on wood-water interactions. Acetylation decreased the strength of the interactions between wood and water as seen from a decrease in differential enthalpy of mixing, both overall and in the dry state. It appears that acetylation removes or hinders the most-energetic interactions or bonding configurations of water in wood, perhaps because acetylation reduces the number of water-accessible hydroxyls more than it reduces the amount of absorbed water molecules.

Keywords Acetylation · Wood · Thermodynamics · Moisture · Enthalpy · Sorption calorimetry

Introduction

The interaction between water molecules and wood has a significant effect on the material properties of wood materials (Carrington 1922; Hiruma 1915; MacLean 1941; Tiemann 1906; Volbehr 1896). Therefore, wood research has strived for more than a century for a better understanding of how water molecules interact with and affect wood (Bowyer 2000). When water molecules are taken up (absorbed) into the solid cell walls, they create space between the wood polymers while interacting with these by hydrogen bonding to the hydroxyl (OH) groups (Chen et al. 2018; Lindh et al. 2017; Matthews et al. 2006). Absorption of water in wood is accompanied by release of heat as a result of the phase change from either liquid or gaseous (vapour) phase to a "sorbed

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state" (Nopens et al. 2019). Conversely, desorption of water consumes heat. Since cell wall water has a lower energy state than liquid water, absorption of water vapour in wood will release more heat than the condensation of vapour to liquid water (Kelly and Hart 1970). The additional energy released from absorption gradually decreases with increasing moisture content, indicating that the difference in energy state between cell wall water and liquid water becomes smaller (Hearmon and Burcham 1955; Kelsey and Clarke 1955, 1956; Nopens et al. 2019). The heat released upon absorption of water in dry wood to reach a certain moisture content is known as the integral enthalpy of mixing (Thybring et al. 2022). This study uses the term "enthalpy of mixing" in line with (Nopens et al. 2019) to highlight that the thermodynamic quantity relates to differences between the liquid and sorbed states, whereas sorption in this study describes the change between gaseous (vapour) and sorbed states.

To characterize the energy state of cell wall water, it is common to examine the derivative of the integral enthalpy of mixing with respect to moisture content, i.e. the differential enthalpy of mixing, $\Delta_{\mathrm{mix}}H$. This parameter can be thought of as the heat released by 1 g of water upon absorption in an infinite mass of wood at a specific moisture content. It can also be interpreted as the energy state of the latest absorbed water molecule at a specific moisture content, assuming that the absorption of a water molecule does not change the state of the already absorbed water or the state of the material. Therefore, characterisation of $\Delta_{\mathrm{mix}}H$ provides a window to understand more about the state of moisture in wood. $\Delta_{\mathrm{mix}}H$ can be determined either by direct experimental calorimetric measurements or derived from an analysis of sorption isotherms at different temperatures using the Clausius–Clapeyron equation (Nopens et al. 2019). Whereas the calorimetric techniques generally yield similar $\Delta_{\mathrm{mix}}H$, the values derived from the Clausius–Clapeyron equation are lower (less negative) at low moisture contents (Nopens et al. 2019), presumably because uncertainty in the sorption isotherm data yields higher uncertainty in $\Delta_{\mathrm{mix}}H$ in the lower moisture range (Thybring et al. 2021).

Another way to gain information about the state of moisture in wood is by manipulation of the wood-water interactions by chemical modifications (Thybring and Fredriksson 2021). These are ways to change the material chemistry, typically to enhance the material properties of wood, e.g. increase the resistance to fire or biological degradation (Zelinka et al. 2022). Acetylation is one such wood modification, where acetic anhydride reacts with hydroxyls within the wood cell wall to replace some of these with acetyl groups (Fuchs 1928; Zelinka et al. 2022). Hereby, the concentration of water-accessible hydroxyls decreases along with the available space for water within cell walls (Awais et al. 2022; Thybring et al. 2020).

Whereas the thermodynamics of moisture sorption in untreated wood has been characterized in several studies by calorimetry (Avramidis and Dubois 1992; Hearmon and Burcham 1955; Kelsey and Clarke 1955, 1956; Nopens et al. 2019; Volbehr 1896) or by sorption isotherm derivation using the Clausius–Clapeyron equation (Esteban et al. 2008a, b; Simón et al. 2015; Stamm and Loughborough 1935), such data for modified wood is very sparse in literature. The only direct calorimetric measurements on modified wood appears to be those obtained by Dieste et al. (2008) on European beech modified by DMDHEU using solution calorimetry which measures the integral enthalpy of mixing. From these data, $\Delta_{\mathrm{mix}}H$ was derived from fits of an assumed exponential model. Furthermore, the Clausius–Clapeyron equation has been applied to derive the differential enthalpy of mixing, $\Delta_{\mathrm{mix}}H$, from sorption isotherm data on the same beech material (Dieste et al. 2008) as well as on Sitka spruce modified in various ways (Yasuda et al. 1995). These data are to the best of our knowledge the only thermodynamic characterisations of moisture in modified wood materials. The results obtained in these two studies show a markedly different behaviour between modifications, in particular below 0.05 g g^{-1} moisture content (see Fig. S1 in the Supplementary Material). However, in this moisture range, uncertainty in sorption isotherm data significantly affects the uncertainty in derived $\Delta_{\mathrm{mix}}H$ values (Thybring et al. 2021).

Instead of deriving $\Delta_{\mathrm{mix}}H$ from fits of mathematical models to either solution calorimetric data or sorption isotherm data, the parameter can be measured directly using sorption calorimetry (Markova et al. 2001; Wadsö and Markova 2000, 2002). This technique has only recently been applied to study water sorption in wood (Nopens et al. 2019), and so far no studies have been done on modified wood materials. Sorption calorimetry works by measuring the heat production rate in two chambers connected by a tube through which water vapour can diffuse. Liquid water is loaded in one chamber while the dry sample material is placed in the other chamber. By evaporation of water and diffusion of vapour through the tube, the relative humidity (RH) is slowly increased in the sample chamber at a rate given by the geometry of the tube. In both chambers, the heat production rate is measured to quantify the amount of water evaporating and the heat released during absorption, respectively. Hereby, the sorption calorimeter allows simultaneous determination of the absorption isotherm and differential enthalpy of mixing, $\Delta_{\mathrm{mix}}H$ (Digaitis et al. 2022; Markova et al. 2001; Wadsö and Markova 2000, 2002).

This study is the first to apply sorption calorimetry to investigate how chemical modification affects wood-water interactions. The aim is to explore how the energy state of absorbed water is influenced by acetylation of the wood cell walls.

Materials and methods

Material preparation

Norway spruce (*Picea abies* (L.) Karst) from an experimental forest in Vindeln, Northern Sweden was used, see more information about the origin in (Fredriksson et al. 2016). From this material, samples of 5×5x10 (longitudinal) mm^3 were cut out and acetylated as part of the study reported by Digaitis et al. (2021). In brief, samples were vacuum dried at 60 °C for 24 h before being vacuum impregnated in a reaction flask with a solution of acetic anhydride and pyridine (1:4 v/v). The flask was subsequently heated at 80 °C in an oilbath for three different reaction times (20 min, 1 h, 3 h) to reach different degrees of acetylation. The use of pyridine ensured a uniform distribution of the acetylation across the cell wall (Digaitis et al. 2021).

Sorption calorimetry

The instrument used for sorption calorimetry was a new, unpublished design with the same principal function as the instruments reported in (Markova et al. 2001; Wadsö and Markova 2000, 2002). Calibration of the calorimeters was done electrically, and the maximal flow rate was determined from calibrations with molecular sieves. Thin pieces of wood that were about 4 mm in length were sliced along the fibre direction using a razor blade. About 50 mg of wood slices were loaded to the sample holder which was transferred to a vacuum oven where the wood was dried at 60 °C for at least 24 h. After drying, the sample holder was removed from the vacuum oven and immediately sealed with aluminum foil. It was then allowed to cool down and the mass of the sample was recorded. After this, the sample holder was attached to the two-chamber calorimetric cell. The instrument was set to a temperature of 25 °C and was left to equilibrate for at least 24 h before water was injected on a hydrophobic membrane in the upper, vaporization chamber to start the measurement. Each measurement lasted approximately 2 days, and after the measurement, the mass was recorded once again.

Data evaluation was done by the basic evaluation procedure described in (Wadsö and Markova 2002), with the addition of the Tian correction for the thermal lag of the instrument. Furthermore, a correction for leakage was made by assuming that the differential enthalpy of mixing should go to zero at high RH. If this was not the case, it was assumed that a constant leakage from the water source occurred throughout the whole measurement. This was corrected for by subtracting the difference between the calorimetric signals at the end of a measurement from the vaporization measurement. This correction had a very small influence of the differential enthalpy of mixing at lower RH that is the main interest of the present work. Moreover, the derived moisture contents for the acetylated samples were corrected for the mass gain from modification. This was done by multiplying the moisture content with $(1+R_{\mathrm{mod}})$ where R_{mod} ($\mathrm{g\ g^{-1}}$) is the mass gain from modification relative to the initial, unmodified mass.

Sorption isotherms

Data for one replicate at 20 °C for the same materials were already available in Digaitis et al. (2021) and could thus be used for comparison to the sorption isotherm data obtained by sorption calorimetry. In addition, data for two replicates of the untreated controls were available from (Thybring and Fredriksson 2024). However, in order to derive $\Delta_{\mathrm{mix}}H$ from the Clausius–Clapeyron equation for comparison with sorption calorimetric data, additional sorption isotherms at 20 °C and 40 °C were determined in two sorption balances (DVS Advantage, Surface

Measurement Systems, UK). To complement the already existing data, one additional replicate at 20 °C and two replicates at 40 °C were determined for the pyridine controls and the acetylated samples with the longest reaction time (3 h). Since these measurements were part of a larger study, both desorption and absorption isotherms were determined although only the absorption isotherms were needed here.

Wood samples were vacuum saturated with water by placing the specimens under vacuum (<2 mbar) in a desiccator for 1 h. Deionised water was then let into the desiccator and finally atmospheric pressure was re-established. A sample was then prepared by cutting small pieces of wood with a razor blade. Any excess surface water was wiped off with a moist Wettex cloth (Freudenberg Home and Cleaning Solutions AB, Malmö, Sweden), and the sample was placed in the sample pan. Each sample was exposed to different RH levels in steps in the sorption balance. Because of the uncertainties with using a mass stability over time criterion to determine when equilibrium was reached (Glass et al. 2018), a fixed time at each step was used. To ensure that sufficient equilibrium was reached at each RH step, the mass change over time was evaluated for each sorption step (see Figs. S6-S8 in the Supplementary Material). The RH generation of the sorption balances was validated using the method described by Wadsö et al. (2009). The desorption isotherm was determined using the following RH-steps with the equilibration time at each step shown in brackets: 95% (60 h), 80% (24 h), 65% (12 h), 50% (12 h), 35% (12 h), 0% (24 h). The absorption isotherm up to 95% was then determined using the same RH steps and equilibration times, except at 95% where the equilibration time was reduced to 24 h. Finally, the dry mass, m_d (g) was determined by using the preheater that exposed the sample to 60 °C/0% RH for 8 h before a temperature stabilisation period of 2 h at 0% RH and the isotherm temperature (20 °C or 40 °C). After this the dry mass was measured. The dry mass range of the various materials was 6.8–10.5 mg. The equilibrium moisture content, u_eq (g g^{-1}), was determined from the equilibrium mass, m_eq, at each RH step as:

$$u_\mathrm{eq} = \frac{m_\mathrm{eq} - m_\mathrm{d}}{m_\mathrm{d}} \tag{1}$$

The equilibrium moisture contents for the acetylated samples were corrected for the mass gain from modification as described for the sorption calorimetry data. The obtained sorption isotherms are shown in Fig. S4 in the Supplementary Material. The absorption isotherms were then used to derive $\Delta_\mathrm{mix}H$ from the Clausius–Clapeyron equation by first fitting the ABC isotherm (Zelinka et al. 2018) to the obtained absorption isotherms. The fit at each temperature was used to determine the RH at specific levels of constant moisture content by interpolation. From these values, the differential enthalpy of mixing was calculated by (Thybring et al. 2022):

$$\Delta_\mathrm{mix}H = R\frac{d\ln\varphi}{d(1/T)}\bigg|_{u_\mathrm{eq}} \tag{2}$$

where R (8.31446 J mol^{-1} K^{-1}) is the gas constant, T (K) is the absolute temperature, and φ (-) is the RH.

Results and discussion

Figure 1 shows the moisture content as function of RH as well as the differential enthalpy of mixing, $\Delta_\mathrm{mix}H$, determined by the sorption calorimeter for the five wood materials. The data has been cut off above 90% RH, since the accuracy of the determined $\Delta_\mathrm{mix}H$ deteriorates at high RH. In Fig. 1a-e the moisture content during measurements is compared with the equilibrium moisture content at 20 °C obtained at five levels of RH determined by Digaitis et al. (2021) with an automated sorption balance. It is seen that the moisture content measured with the sorption calorimeter is lower than the equilibrium moisture content, and that the isotherms measured by the sorption calorimeter do not start at zero RH. This is also clear from Fig. S2 in the Supplementary Material which shows that the moisture content was, in relative terms, fairly consistently about 30% lower than the equilibrium moisture content at a given RH. The reason for this discrepancy is likely that during the dynamic RH measurements in the sorption calorimeter, the wood is further from equilibrium than in the sorption measurements at constant RH in the automated sorption balance. The RH is thus an uncertain parameter in the sorption calorimetric measurement for samples exhibiting slow sorption. Note that in the sorption calorimeter it

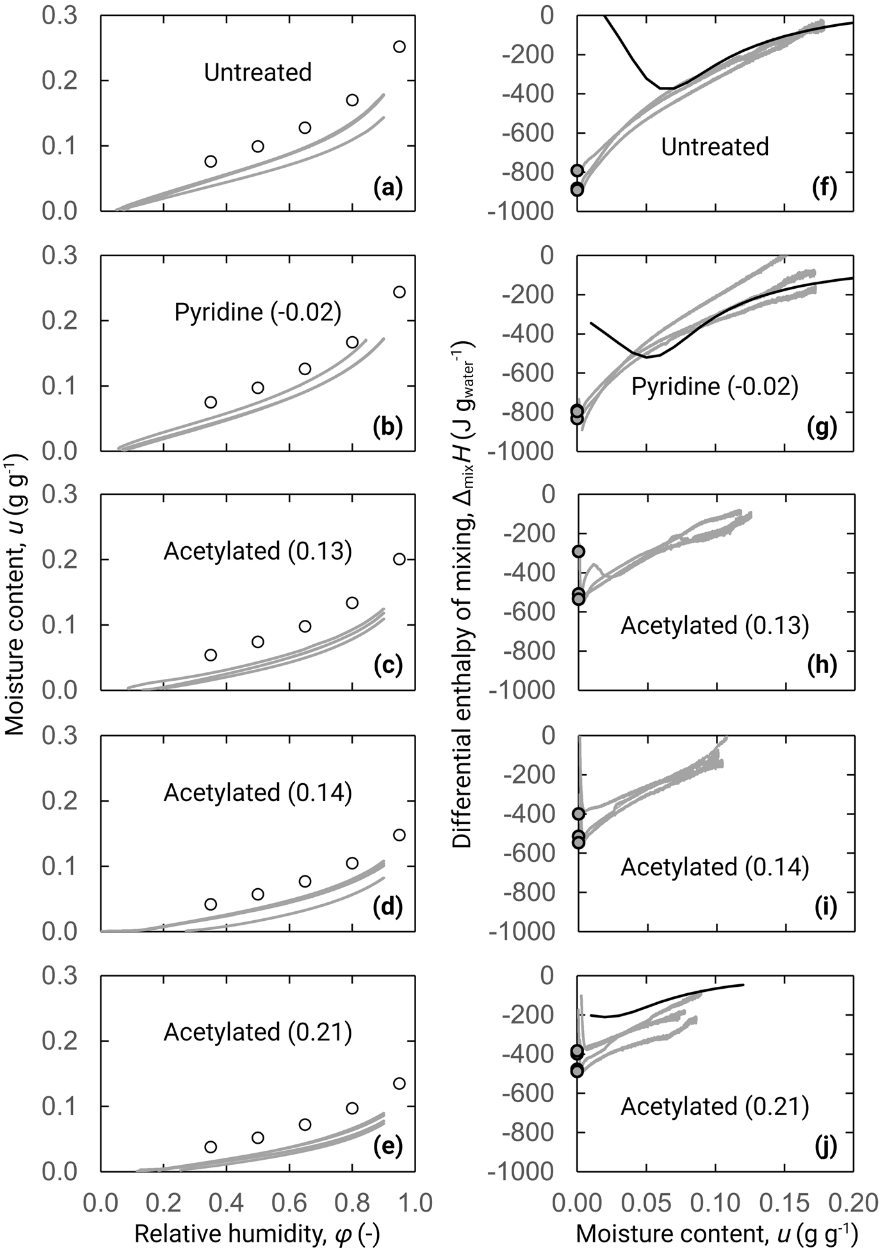

Fig. 1 **a-e** Moisture content during sorption calorimetric measurements (grey lines) compared with absorption isotherms determined gravimetrically (black circles) in an automated sorption balance (Digaitis et al. 2021). **f-j** Differential enthalpy of mixing, $\Delta_{mix}H$, as function of moisture content for the five different wood materials (grey lines). Numbers in parentheses mark the mass gain from modification, R_{mod} (g g^{-1}). Filled circles illustrate the extrapolated $\Delta_{mix}H$ in the dry state, i.e. at 0 g g^{-1} moisture content. The black lines describe the differential enthalpy of mixing derived from the Clausius–Clapeyron equation for gravimetric absorption data for the same materials at 20 °C and 40 °C using an automated sorption balance. For all plots, the sorption calorimetric data have been cut off above 90% RH, and the moisture contents for the acetylated wood have been corrected for mass gain from modification (R_{mod})

is the sample itself that, by absorbing water vapour, generates the flow from the water source; in a sorption balance the RH is controlled by the instrument and can be kept constant until equilibrium is reached. However, in the sorption calorimeter, the determined moisture content and the differential enthalpy of mixing are robust parameters that do not rely on the RH of the sorption calorimeter. When water diffuses from the water source to the sample, this flow rate is accurately measured, and when the water molecules interact with the wood material, the produced heat is accurately measured. The diagrams of Fig. 1f-j are therefore more accurate than the sorption isotherms of Fig. 1a-e, and the differential enthalpy of mixing at zero moisture content should be well determined.

Figure 1f-j shows the differential enthalpy of mixing, $\Delta_{mix}H$, as function of the moisture content during measurements. Lower (less negative) initial values of $\Delta_{mix}H$ at low moisture contents can be seen for the acetylated wood compared to untreated and pyridine controls. For these latter two materials, the enthalpy curves correspond well with those derived using the Clausius–Clapeyron equation, Eq. (2), on absorption data, except below 0.05 g g^{-1}. As previously discussed (see Introduction section), the results derived with the Clausius–Clapeyron equation from sorption isotherm data are uncertain in the low moisture range (Thybring et al. 2021).

The decreasing $\Delta_{\text{mix}}H$ with increasing moisture content could be interpreted as a result of sequential absorption of water molecules at the most energetic sorption sites before less-energetic sites are occupied. Alternatively, the decrease could be explained by progressively decreasing ordering of the water molecules as their concentration increases. Results from molecular dynamics simulations of a cellulose-hemicellulose system indicate that water molecules at low moisture content are preferentially absorbed in free volume voids in the hemicellulose (Kulasinski et al. 2015). This is in line with experimental results showing a lower swelling at low moisture contents, indicating absorption of water into free volume voids (Arzola-Villegas et al. 2019). As the moisture content increases, the computer simulations show water molecules accumulating at the interface between cellulose and hemicellulose. Importantly, the ordering of the absorbed water molecules is seen to decrease as the moisture content increases (Kulasinski et al. 2015), indicating that the water molecules adopt less favourable bonding configurations. This makes sense when considering that absorbed water molecules increasingly have to interact with other water molecules as their concentration increases. These molecules create space within the cell walls and may form a percolated network of water as well as water clusters at high moisture contents (Arzola-Villegas et al. 2019). Therefore, absorption of water could lead to a gradual change in bonding configuration of water molecules and sorption sites as more and more water is accommodated in the cell walls. Hereby, the decreasing $\Delta_{\text{mix}}H$ with increasing moisture content could be a result of lower overall energy in the bonding configurations adopted as more water molecules need to fit into the cell walls. This interpretation also fits with the observation that the entropy of mixing as derived from sorption isotherm data decreases with increasing moisture content (Ouertani et al. 2014; Stamm and Loughborough 1935). By extrapolation to zero moisture content, the $\Delta_{\text{mix}}H$ in the dry state was estimated and plotted in Figs. 1f-j and 2a. For untreated and pyridine controls, values around -800 J g$_{\text{water}}{}^{-1}$ to -850 J g$_{\text{water}}{}^{-1}$ were found which equals -14.5 kJ mol^{-1} to -15.5 kJ mol^{-1}. This corresponds rather well with $\Delta_{\text{mix}}H$ values for natural polymers in the dry state of approximately -18 kJ mol^{-1} (Kocherbitov et al. 2004, 2010, 2008; Wojtasz et al. 2016). For the acetylated wood, $\Delta_{\text{mix}}H$ in the dry state falls around -440 J g$_{\text{water}}{}^{-1}$ to -500 J g$_{\text{water}}{}^{-1}$ corresponding to -7.9 kJ mol^{-1} to -9 kJ mol^{-1}. Thus, the first water molecules absorbed into the modified wood have a markedly weaker interaction with the cell wall polymers. This might be a result of fewer high-energy sorption sites, less energetically favourable bonding configurations with the fewer water-accessible hydroxyls (Fig. 2a) or less free volume voids present in the modified cell walls.

By integrating $\Delta_{\text{mix}}H$ from the dry state to 90% RH, the integral enthalpy of mixing is obtained describing the total energy released over this moisture range per gram dry material (Fig. 2b). The integral enthalpy of mixing at 90% RH is seen to decrease from around -65 J g$_{\text{dry}}{}^{-1}$ for untreated and pyridine controls to around -20 J g$_{\text{dry}}{}^{-1}$ to -30 J g$_{\text{dry}}{}^{-1}$ for acetylated wood. This reduction is both because of a lower $\Delta_{\text{mix}}H$ in the dry state and a lower absorbed moisture content at 90% RH (Fig. 2b). When normalizing the integral enthalpy of mixing with the moisture content at 90% RH, the acetylated wood yields values around -250 J g$_{\text{water}}{}^{-1}$ (-4.7 kJ mol^{-1}) compared with around -385 J g$_{\text{water}}{}^{-1}$ (-6.9 kJ mol^{-1}) for untreated and pyridine controls. This change in normalized integral enthalpy points to a change in the average energy of interaction between the absorbed water and the modified cell walls.

Figure 3 shows the $\Delta_{\text{mix}}H$ curves for the acetylated wood right-shifted on the moisture axis by an amount corresponding to the average reduction in moisture content at 90% RH. Interestingly, it can be seen that for the lower degrees of acetylation, i.e. R_{mod} of 0.13–0.14 g g^{-1}, the shifted enthalpy curves are well aligned with the later parts of the enthalpy curves for untreated and pyridine controls. The enthalpy curves for the wood with the highest degree of acetylation of $R_{\text{mod}} = 0.21$ g g^{-1}, do not align fully with those of the untreated and pyridine controls, even though the overall inclination is similar (Fig. 3c). Thus, it appears that the first part of the

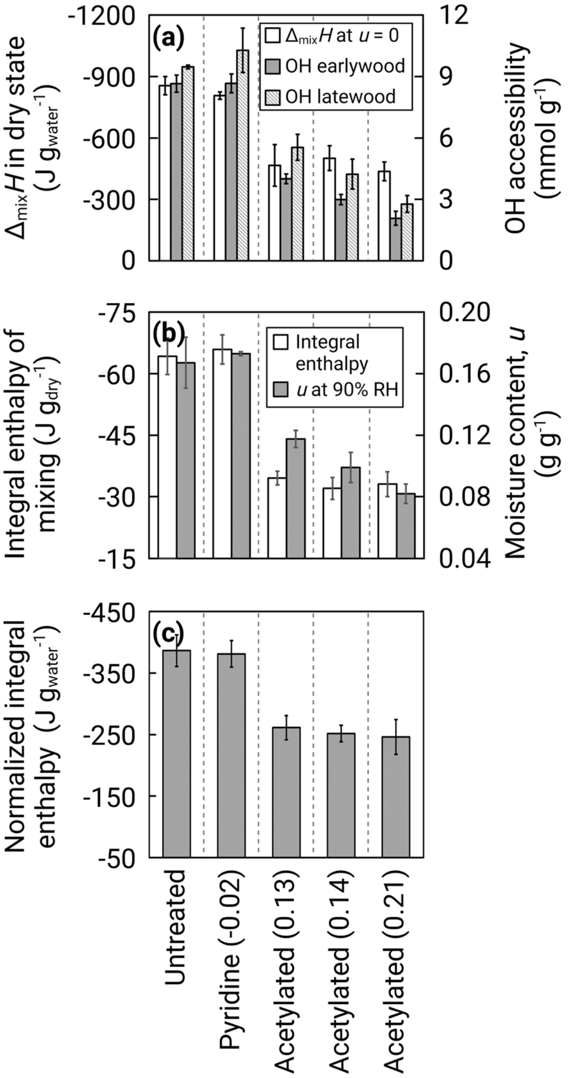

Fig. 2 **a** Extrapolated differential enthalpy of mixing in the dry state (white) for the five wood materials. Also plotted is the gravimetrically determined hydroxyl accessibility in earlywood (grey) and latewood (hatched) from (Digaitis et al. 2021) for the same materials. **b** Integral enthalpy of mixing (white) and moisture content (grey) at 90% RH from sorption calorimetric measurements for the five wood materials. **c** Integral enthalpy of mixing at 90% RH normalised with the moisture content at 90% RH from sorption calorimetric measurements. Numbers in parentheses mark the mass gain from modification, R_{mod} (g g^{-1}). Moisture contents and integral enthalpy of mixing for acetylated wood have been corrected for mass gain from modification (R_{mod})

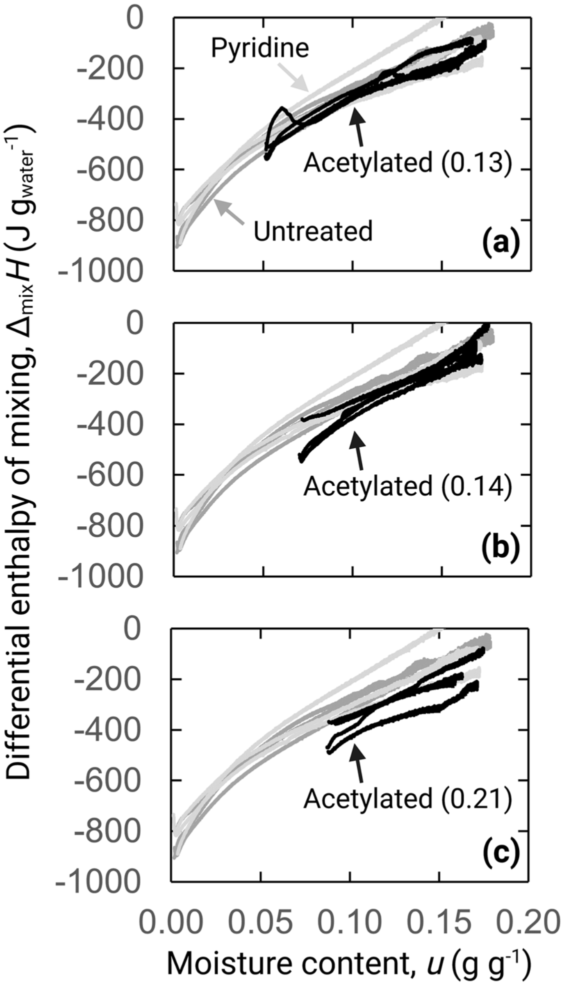

Fig. 3 Differential enthalpy of mixing of untreated and acetylated wood with a mass gain from modification, R_{mod} of **a** 0.13 g g^{-1}, **b** 0.14 g g^{-1}, and **c** 0.21 g g^{-1}. For the latter three materials, the curves have been horizontally shifted to the right by 0.050 g g^{-1}, 0.068 g g^{-1}, and 0.085 g g^{-1}, respectively, corresponding to the average difference in moisture content in the sorption calorimetric measurements between the untreated and respective acetylated samples at 90% RH

enthalpy curve in untreated wood has been removed by acetylation, indicating a correlation between moisture reduction and the highest (most negative) values of $\Delta_{mix}H$. This could be interpreted as progressive removal of the sorption sites with highest energy by acetylation. However, the reduction in moisture content does not scale with the removal of water-accessible hydroxyls, since the number of hydroxyls that are removed or shielded by acetylation is about 40–80% higher than the number of water molecules excluded from the cell walls (Table S3 in the Supplementary Material). This is in line with the results of Thybring et al. (2020) which show that the reduction of moisture content by wood modification is correlated with the reduction in available space for water within cell walls, independently of the change in hydroxyl accessibility. This means that with an increasing degree of acetylation, fewer hydroxyls are available for interacting with the absorbed water, both in absolute numbers and relative to the amount of water molecules present, than in untreated wood. Therefore, the number of interactions with hydroxyls per absorbed water molecule is less in the acetylated wood than in the untreated wood. This could mean that high-energy interactions with specific hydroxyls are hindered by acetylation as well as energetically favourable bonding configurations of the absorbed water molecules. In fact, it appears that acetylation lowers the entropy of mixing similar to the effect of other types of modification, see Figs. S2 and S7 in the Supplementary Material. In future work, it could be interesting to explore different chemical modifications that affect the hydroxyl accessibility and moisture reduction independently (Thybring et al. 2020).

Conclusion

This study is the first to use sorption calorimetry for exploring the effect of chemical modification on wood-water interactions. Acetylation decreased the strength of the wood-water interaction which was shown by a decrease in differential enthalpy of mixing, both overall and in the dry state. It appears that acetylation removes or hinders the most-energetic interactions or bonding configurations of water in wood, perhaps because acetylation reduces the number of water-accessible hydroxyls more than it reduces the amount of absorbed water molecules.

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Author contributions M.F., L.W. and R.D. conducted the experiments, E.E.T. and L.W. analysed the data, E.E.T. prepared the figures and wrote the original draft of the manuscript. All authors reviewed and edited the manuscript.

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Data availability Data available at https://doi.org/10.17894/ucph.2463c234-cdcc-40c2-9dc1-f5917acab157.

Declarations

Ethical approval Not applicable.

Competing interests The authors declare no competing interests.

References

Arzola-Villegas X, Lakes R, Plaza NZ, Jakes JE (2019) Wood moisture-induced swelling at the cellular scale—ab intra. Forests 10:996

Avramidis S, Dubois F (1992) Sorption energies of some Canadian species. Holzforschung 46:177–179

Awais M et al (2022) Wood–water relations affected by anhydride and formaldehyde modification of wood. ACS Omega 7:42199–42207. https://doi.org/10.1021/acsomega.2c04974

Bowyer JL (2000) Wood science in a changing world – Where are we headed? Wood Sci Technol 34:175–181. https://doi.org/10.1007/s002260000049

Carrington H (1922) The elastic constants of spruce as influenced by moisture content. Aeronaut J 26:462–471

Chen M, Coasne B, Guyer R, Derome D, Carmeliet J (2018) Role of hydrogen bonding in hysteresis observed in sorption-induced swelling of soft nanoporous polymers. Nat Commun 9:3507. https://doi.org/10.1038/s41467-018-05897-9

Dieste A, Krause A, Militz H (2008) Modification of Fagus sylvatica (L.) with 1,3-dimethylol-4,5-dihydroxyethylene urea (DMDHEU): part 1. Estimation of heat adsorption by the isosteric method (Hailwood-Horrobin model) and by solution calorimetry. Holzforschung 62:577–583

Digaitis R, Falkman P, Oltner V, Briggner LE, Kocherbitov V (2022) Hydration and dehydration induced changes in porosity of starch microspheres. Carbohyd Polym 291:119542. https://doi.org/10.1016/j.carbpol.2022.119542

Digaitis R, Thybring EE, Thygesen LG, Fredriksson M (2021) Targeted acetylation of wood: a tool for tuning wood-water interactions. Cellulose 28:8009–8025. https://doi.org/10.1007/s10570-021-04033-z

Esteban LG, de Palacios P, Fernández FG, Guindeo A, Cano NN (2008a) Sorption and thermodynamic properties of old and new Pinus sylvestris wood. Wood Fiber Sci 40:111–121

Esteban LG, de Palacios P, Fernandez FG, Guindeo A, Conde M, Baonza V (2008b) Sorption and thermodynamic properties of juvenile Pinus sylvestris L. wood after 103 years of submersion. Holzforschung 62:745–751. https://doi.org/10.1515/hf.2008.106

Fredriksson M, Wadsö L, Johansson P, Ulvcrona T (2016) Microclimate and moisture content profile measurements in rain exposed Norway spruce (*Picea abies* (L.) Karst.) joints. Wood Material Sci Eng 11:189–200. https://doi.org/10.1080/17480272.2014.965742

Fuchs W (1928) Zur Kenntnis des genuinen Lignins, I.: Die Acetylierung des Fichtenholzes. Ber Dtsch Chem Ges (A B Ser) 61:948–951. https://doi.org/10.1002/cber.19280610512

Glass SV, Boardman CR, Thybring EE, Zelinka SL (2018) Quantifying and reducing errors in equilibrium moisture content measurements with dynamic vapor sorption (DVS) experiments. Wood Sci Technol 52:909–927. https://doi.org/10.1007/s00226-018-1007-0

Hearmon RFS, Burcham JN (1955) Specific heat and heat of wetting of wood. Nature 176:978–978

Hiruma J (1915) Experiment of the electric resistance in wood. In: extracts from the bulletin of the forest experiment station, Meguro, Tokyo. Bureau of forestry, department of agriculture and commerce, Tokyo, Japan, pp 59–65

Kelly MW, Hart CA (1970) Water vapor sorption rates by wood cell walls. Wood Fiber Sci 1:270–282

Kelsey KE, Clarke LN (1955) Effect of temperature and initial moisture content on the heat of wetting of wood. Nature 176:83–84. https://doi.org/10.1038/176083a0

Kelsey KE, Clarke LN (1956) The heat of sorption of water by wood. Aust J Appl Sci 7:160–175

Kocherbitov V, Arnebrant T, Söderman O (2004) Lysozyme−water interactions studied by sorption calorimetry. J Phys Chem B 108:19036–19042. https://doi.org/10.1021/jp0476388

Kocherbitov V, Ulvenlund S, Briggner L-E, Kober M, Arnebrant T (2010) Hydration of a natural polyelectrolyte xanthan gum: comparison with non-ionic carbohydrates. Carbohyd Polym 82:284–290. https://doi.org/10.1016/j.carbpol.2010.04.055

Kocherbitov V, Ulvenlund S, Kober M, Jarring K, Arnebrant T (2008) Hydration of microcrystalline cellulose and milled cellulose studied by sorption calorimetry. J Phys Chem B 112:3728–3734. https://doi.org/10.1021/jp711554c

Kulasinski K, Guyer R, Derome D, Carmeliet J (2015) Water adsorption in wood microfibril-hemicellulose system: Role of the crystalline–amorphous interface. Biomacromol 16:2972–2978. https://doi.org/10.1021/acs.biomac.5b00878

Lindh EL, Terenzi C, Salmen L, Furo I (2017) Water in cellulose: evidence and identification of immobile and mobile adsorbed phases by 2H MAS NMR. Phys Chem Chem Phys 19:4360–4369. https://doi.org/10.1039/C6CP08219J

MacLean JD (1941) Thermal conductivity of wood. Heat Piping Air Cond 13:380–391

Markova N, Sparr E, Wadsö L (2001) On application of an isothermal sorption microcalorimeter. Thermochim Acta 374:93–104. https://doi.org/10.1016/S0040-6031(01)00476-2

Matthews JF et al (2006) Computer simulation studies of microcrystalline cellulose I beta. Carbohyd Res 341:138–152

Nopens M, Wadsö L, Ortmann C, Fröba M, Krause A (2019) Measuring the heat of interaction between lignocellulosic materials and water. Forests 10:674

Ouertani S, Azzouz S, Hassini L, Koubaa A, Belghith A (2014) Moisture sorption isotherms and thermodynamic properties of Jack pine and palm wood: Comparative study. Ind Crops Prod 56:200–210. https://doi.org/10.1016/j.indcrop.2014.03.004

Simón C, Esteban LG, de Palacios P, Fernández FG, Martín-Sampedro R, Eugenio ME (2015) Thermodynamic analysis of water vapour sorption behaviour of juvenile and mature wood of Abies alba Mill. J Mater Sci 50:7282–7292. https://doi.org/10.1007/s10853-015-9283-7

Stamm AJ, Loughborough WK (1935) Thermodynamics of the swelling of wood. J Phys Chem 39:121–132

Thybring EE, Boardman CR, Zelinka SL, Glass SV (2021) Common sorption isotherm models are not physically valid for water in wood. Colloids Surf, A 627:127214. https://doi.org/10.1016/j.colsurfa.2021.127214

Thybring EE, Fredriksson M (2021) Wood modification as a tool to understand moisture in wood. Forests 12. https://doi.org/10.3390/f12030372

Thybring EE, Fredriksson M (2024) How accurate are automated sorption balances? An analysis of errors in wood moisture content from uncertainties in the conditioning environment. Dry Technol 42:372–379. https://doi.org/10.1080/07373937.2023.2294021

Thybring EE, Fredriksson M, Zelinka SL, Glass SV (2022) Water in wood: a review of current understanding and knowledge gaps. Forests 13. https://doi.org/10.3390/f13122051

Thybring EE, Piqueras S, Tarmian A, Burgert I (2020) Water accessibility to hydroxyls confined in solid wood cell walls. Cellulose 27:5617–5627. https://doi.org/10.1007/s10570-020-03182-x

Tiemann HD (1906) Effect of moisture upon the strength and stiffness of wood vol Bulletin 70. US department of agriculture, forest service, Washington, DC, USA

Volbehr BFKJ (1896) Untersuchungen über die Quellung der Holzfaser. Universität Kiel

Wadsö L, Anderberg A, Åslund I, Söderman O (2009) An improved method to validate the relative humidity generation in sorption balances. Eur J Pharm Biopharm 72:99–104. https://doi.org/10.1016/j.ejpb.2008.10.013

Wadsö L, Markova N (2000) A double twin isothermal microcalorimeter. Thermochim Acta 360:101–107. https://doi.org/10.1016/S0040-6031(00)00574-8

Wadsö L, Markova N (2002) A method to simultaneously determine sorption isotherms and sorption enthalpies with a double twin microcalorimeter. Rev Sci Instrum 73:2743–2754

Wojtasz J, Carlstedt J, Fyhr P, Kocherbitov V (2016) Hydration and swelling of amorphous cross-linked starch microspheres. Carbohyd Polym 135:225–233. https://doi.org/10.1016/j.carbpol.2015.08.085

Yasuda R, Minato K, Norimoto M (1995) Moisture adsorption thermodynamics of chemically-modified wood. Holzforschung 49:548–554

Zelinka SL et al (2022) Review of wood modification and wood functionalization, technologies. Forests 13:1004. https://doi.org/10.3390/f13071004

Zelinka SL, Glass SV, Thybring EE (2018) Myth versus reality: do parabolic sorption isotherm models reflect actual wood–water thermodynamics? Wood Sci Technol 52:1701–1706. https://doi.org/10.1007/s00226-018-1035-9