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ORIGINAL PAPER

Moisture adsorption of glucomannan and xylan hemicelluloses

Karol Kulasinski · Lennart Salmén · Dominique Derome · Jan Carmeliet

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Abstract Wood and wood materials are highly sensitive to moisture in the environment. To a large extent this relates to the hygroscopicity of wood hemicelluloses. In order to increase our understanding of the effects of moisture sorption of the major wood hemicelluloses, glucomannan and xylan, model experiments using films of amorphous konjak glucomannan and rye arabinoxylan were conducted. Moisture-induced expansion and stiffness softening were characterized using dynamic mechanical testing. Both hemicelluloses showed a threshold around 5 % of moisture content above which swelling increased whereas the modulus decreased by more than 70 %. FTIR spectra, using H_2O and D_2O, indicated that even at high RH about 15 % of the hydroxyl groups were not accessible to hydrogen exchange by D_2O. For xylan both hydroxyl groups were found to exchange in the same manner while for the glucomannan the O(6)H group seemed to be the most accessible.

Keywords Deuterium · Glucomannan · Hemicellulose · Sorption · Swelling · Weakening · Xylan

K. Kulasinski (✉) · J. Carmeliet
Chair of Building Physics, Swiss Federal University of Technology Zurich, Stefano-Franscini-Platz 5,
8093 Zurich, Switzerland
e-mail: kulasinski@gmail.com

K. Kulasinski · D. Derome · J. Carmeliet
Laboratory for Multiscale Studies in Building Physics of Building Science and Technology, Empa, Swiss Federal Laboratories for Materials Science and Technology,
Überlandstrasse 129, 8600 Dübendorf, Switzerland

L. Salmén
Innventia, Box 5604, SE-114 86 Stockholm, Sweden

Introduction

Hemicelluloses play an important role in the structure of the cell wall of plants (Kollmann and Cote 1968; Cousins 1978; Salmén 2015). In the cell wall hemicelluloses may be considered to function as an adhesive between the stiff reinforcing cellulose microfibrils and the matrix lignin (Salmén and Burgert 2009). The hemicelluloses are also important in the formation of the cell wall as they provide an important media for the excreted cellulose molecules to form into the partly crystalline microfibrils (Atalla et al. 1993; Terashima et al. 2009). The hemicelluloses are highly hygroscopic and are in their living cell wall environment in an amorphous state (Cousins 1978; Olsson and Salmén 2004; Kulasinski et al. 2015). Thus they provide for a high flexibility of the fibre cell wall. In the utilization of wood materials or cellulosic products made thereof, the moisture sensitivity of these hemicelluloses often poses a problem in that the stiffness of materials is lost or that dimensional changes due to swelling induces cracks. Thus there is a high interest in increasing the knowledge regarding the interactions of moisture with various hemicelluloses (Bergander and Salmén 2002).

In wood there are mainly two types of hemicelluloses existing: in softwood O-acetyl-galactoglucomannan and arabino-4-O-methylglucoronoxylan and in hardwood O-acetyl-4-O-methylglucoronoxylan with minor contents of glucomannan (Dinwoodie 2000). In terms of moisture sorption these structures mainly differ in the number of hygroscopic hydroxyl groups. The glucomannans have three hydroxyl groups per carbohydrate unit of either glucose or mannose and xylan two hydroxyl groups per xylose unit. In general, there exists a lot of experimental and mechanical studies regarding the sorption behavior of moisture on carbohydrates (Cousins 1978; Olsson and Salmén 2003, 2004; Charlier and Mazeau 2012; Rissanen et al. 2014; Kulasinski et al. 2015). Hemicelluloses follow the general pattern of a sigmoidal sorption with increasing relative humidity, RH. At higher RH the presence of charged groups on specific hemicelluloses may contribute to sorption, rendering an even higher increased moisture uptake (Berthold et al. 1996). However, although moisture plays an essential role for the properties of wood hemicelluloses, not much detailed studies regarding the interaction between these hemicelluloses and moisture has been performed.

In order to increase the understanding regarding the effects of moisture sorption of wood, hemicelluloses of glucomannan and xylan model experiments utilizing accessible hemicellulose representatives of these two types of hemicelluloses, namely a konjac glucomannan and a rye arabinoxylan, have been performed. The sorption behavior of these two hemicelluloses was investigated for both in an atmosphere of normal water as well as with the utilization of FTIR in heavy water to provide molecular information regarding the sorption sites.

Materials and methods

A commercial glucomannan extracted from *Amorphophallus Konjac* (kGM) with a ratio of glucose to mannose of 2/3 and a molecular weight of 35,000 g/mol was utilized. Films cast from an aqueous solution with a thickness of 0.01 mm (Fig. 1a) were made.

Rye arabinoxylan (rAX), from Megazyme International Ireland Ltd., Bray, Co. Wicklow, Ireland, with a ratio of arabinose to xylan of 1/2 and a molecular weight of 290,000 g/mol was utilized. Films were prepared by moistening 1 g of rye arabinoxylan flour with 10 ml of 95 % ethanol and dissolved in 35 ml of deionized water by heating at 100 °C under magnetic stirring for 30 min. The xylan solution was allowed to cool down to room temperature and then placed in a polystyrene Petri dish, 14 cm in diameter, and dried in an oven at 30 °C for 24 h (Fig. 2b). The resulting film had a thickness of 0.02 mm.

DVS

Moisture sorption isotherms from 0 to 90 %RH at 30 °C were determined utilizing a Dynamic Vapor Sorption (DVS) equipment from Surface Measurement Systems Ltd. This device generates a moist atmosphere by mixing dry and saturated air streams generated at a constant temperature. A microbalance registers the mass changes throughout the sorption process. The amount of water is given as moisture ratio, m, as gram water per gram dry material. Films of about 1 mg in the form of strips were used. Samples were dried at RH = 0 % until no weight loss was detected and then tested according to the following RH series: 0–10–40–70–90–70–40–10–0 % RH. The duration of each step was 500 min for a total time of 82 h.

DMA

Moisture expansion and viscoelastic properties as a function of RH were measured on a dynamic mechanical analyzer, DMA, from TA instruments (Q800 with RH accessory). The humidity generator mixes dry and water-saturated streams to give a chosen RH. The hemicellulose film samples were cut in 25 × 8 mm^2 rectangles, mounted between the clamps and exposed to changing RH (0–90 %) in 2 % steps with 15 min equilibration per step at a temperature of 25 °C. The expansion of films was measured by applying a constant minimal force of 0.01 N (to keep the sample flat) and recording the strain, i.e. elongation of the film divided by its initial length. The dynamic elastic modulus and tan(d) was alternatively monitored by applying a dynamic strain of 0.2 % at a frequency of 1 Hz at a constant load of 120 % of the dynamic load.

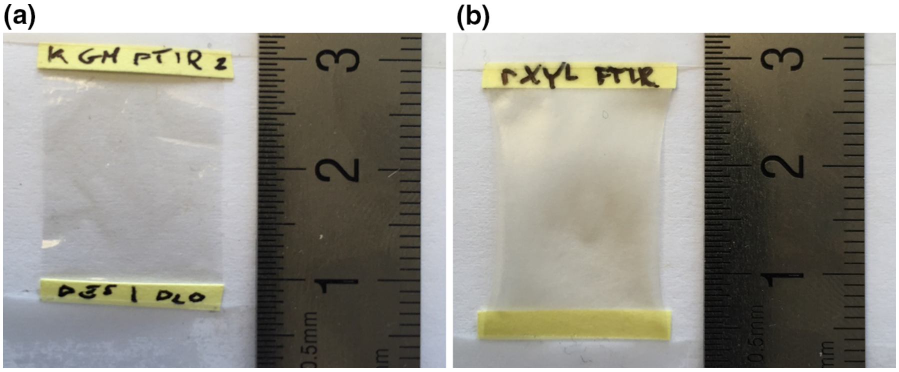
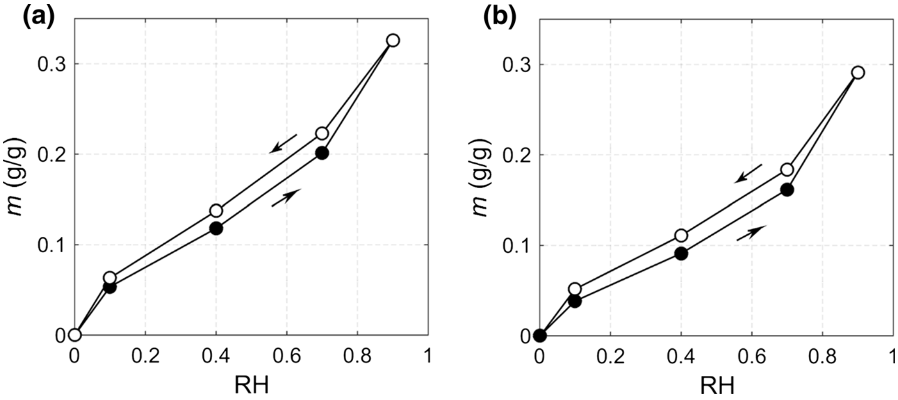


Fig. 1 Test samples of **a** glucomannan and **b** arabinoxylan films

Fig. 2 Moisture sorption *curves*, showing hysteresis, of **a** glucomannan and **b** arabinoxylan at 30 °C



FTIR

Absorbance spectra in transmission were recorded with a Varian 680-IR spectrometer (Varian AB). The sample was mounted in a temperature-controlled chamber with zinc selenide glasses placed in the beam path in order to change the atmosphere around the sample. Air at controlled temperature and relative humidity was circulated through the chamber throughout the IR measurements. The atmosphere was generated by mixing dry air and moisture-saturated air in a VTI RH-200 apparatus.

Heavy (D_2O) water was used for vapor generation. Measurements were made in the range from 0 to 90 % RH at a temperature of 25 °C. In order to maintain a constant low load to counteract the expansion or contraction of the films with changes in moisture content, the position of the clamps holding the films were adjusted manually such that an identical stress of 10 MPa was constantly applied. Spectra with non-polarized light were recorded in the wavenumber range from 500 to 4000 cm^{-1} by a Mercury-Cadmium-Telluride (MCT) detector cooled with liquid nitrogen. The resolution of the spectra was 4 cm^{-1}. The background spectra of D_2O were recorded with the same atmosphere as that used in the sorption experiment, for the effects of the moisture in the air around the tested samples to be taken into account. The samples were first dried overnight. Spectra of the hemicellulose films, in equilibrium with the surrounding atmosphere, were obtained after conditioning for 120 min at each relative humidity as mean spectra calculated over a 30 s period. The spectra were baseline-corrected at the wavenumbers 1795, 2075, 2750, 3035, 3680, and normalized to 1 at 1385 cm^{-1}, the major absorbance peak reflecting the carbohydrate backbone. The absorption of moisture and the exchange on the hydroxyls from OH to OD was determined as the difference between the measured spectrum and the base spectrum taken at an atmosphere of 0 % RH. Peak areas for each characteristic band was monitored noticing that the band widths are constant for all the RH levels studied. (Olsson and Salmén 2004).

Results

Adsorption isotherms

The adsorption and desorption curves of the two types of hemicelluloses are shown in Fig. 2. The results were obtained by testing one sample of each hemicellulose. A typical sigmoidal shape was observed with a hysteresis of 3–4 % of moisture content. The shape of the curves differs between the two hemicelluloses, as the glucomannan was characterized by a slightly higher moisture sorption capacity at all RHs. The observed differences are rather small and should be regarded as examples of the two hemicelluloses. The differences in moisture adsorption would mainly depend on the degree of substitution of each hemicellulose and may thus vary slightly between different types of these hemicelluloses.

Mechanical effects

The moisture expansion of the films during sorption is shown in Fig. 3a. During testing, the films of hemicellulose were kept flat by applying a small force, however due to internal relaxation processes and resulting bending of the films, the strain could not be determined above $m = 0.15$. The larger expansion of the xylan film as compared to the glucomannan was presumably related to different degrees of expansion in the different orientations as the volumetric swelling of these amorphous films should be closely related to the volume of the absorbed moisture (Salmén and Fellers 1989). It is noticeable that for both xylan and glucomannan the expansion increased (change in slope) above a moisture content of about 0.09 although this corresponded to different RH for the two materials and it could indicate the onset of a moisture-induced transition.

In Fig. 3b, the relative dynamic elastic modulus is given as a function of moisture content for the two hemicelluloses. The dry values of glucomannan and xylan were to be 4.7 and 4.3 GPa, respectively; in the same range as noted by others (Cousins 1978; Stevanic et al. 2011). Similar to what is seen for wood, the decrease of the modulus of both hemicelluloses were characterized by a threshold located around $m = 0.05$. An increase of the modulus by 10 % was observed at the early stage of adsorption (Fig. 3b) presumably due to release of internal stresses resulting in a more uniform loading of the films. Compared to the dry value, the hemicelluloses at high moisture content lost about one order of magnitude of their stiffness. In this sense the results were similar to those obtained by Cousins (1978) for both xylan and glucomannan although in our case the onset of softening occurred at somewhat lower moisture contents. For both hemicelluloses most of the weakening, took place in the range of 0.05–0.15 moisture content. The weakening of the rAX could perhaps be said to appear at an earlier stage of adsorption compared to kGM, i.e. 0.03 vs. 0.05. Figure 3c shows the $\tan(\delta)$ value as a function of moisture content for the two hemicelluloses. It can be clearly seen that the ratio between loss and storage modulus increases for both hemicelluloses, in particular for $m > 15$ %, which complements other experiments in showing the softening process advancing with moisture content (Olsson and Salmén 2003). For both hemicelluloses the appearance of a secondary transition around $\mathrm{m} = 10$ % was obvious similar to what has previously been noted (Olsson and Salmén 2003).

Molecular effects

In Fig. 4 typical FTIR spectra of partly deuterium exchanged hemicellulose films are shown. The measured spectra have two regions of interest, the OH and OD peaks found in the range $\nu = 3000–3700\ \mathrm{cm}^{-1}$ and $\nu = 2200–2700\ \mathrm{cm}^{-1}$, respectively.

In order to monitor the deuterium exchange process difference spectra related to the original dry non-deuterium exchanged sample was calculated (Fig. 5a) showing the process from dry to the highest absorption at 90 % D_2O followed by the drying process of decreasing D_2O RH down to the subsequent new dry state. Upon D_2O adsorption, the OD peaks were increasing both due to an exchange of hydroxyl OH-groups to OD-groups as well as due to absorption of D_2O reaching a maximum of the OD peaks at an RH of 90 %. After that, during the desorption process, the OD peaks diminished until only the exchanged hydroxyl groups were visible at the new dry state. The evaluation of the OH peaks showed on the other hand only a decrease due to the exchange process.

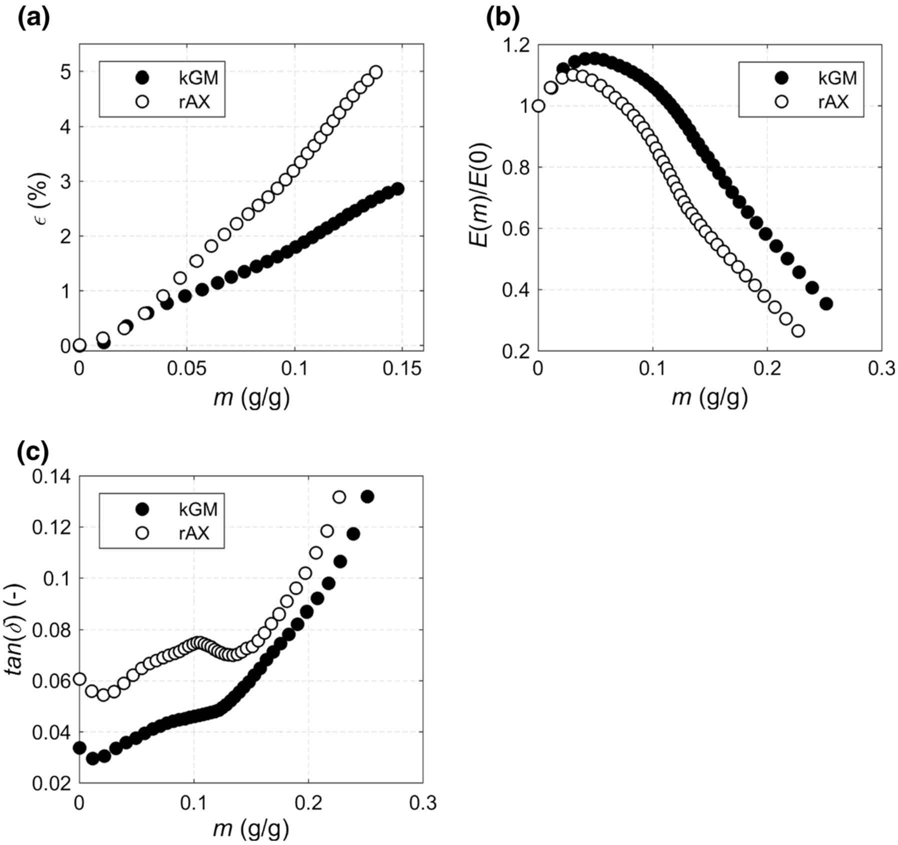


Fig. 3 **a** Moisture expansion, **b** relative dynamic elastic modulus and **c** tan delta as a function of moisture content at 25 °C

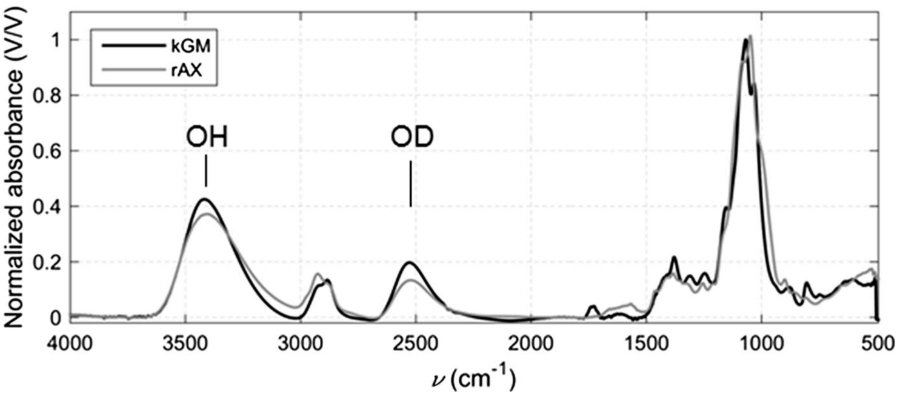


Fig. 4 FTIR spectrum of partly deuterium-exchanged films of arabinoxylan and glucomannan

These phenomena are more clearly illustrated in Fig. 5b, c showing the evolution of the peak areas for the OH and OD peaks of the arabinoxylan and the glucomannan respectively. The exchange process was similar for both hemicelluloses, with the largest change occurring for $m < 10$ %, reflecting both the exchange process and the absorption of D_2O. It is surprising that the peak areas changed so little at the higher RH a phenomenon though earlier observed for cellulosic samples (Olsson and Salmén 2004). During desorption the decreased content of absorbed D_2O was reflected in a decrease of the OD peaks. The OH peaks stayed for both hemicelluloses constant until low RH (RH $<$ 10 %) was reached when a small increase occurred. This increase was presumably related to a small re-exchange of OD groups to OH groups due to

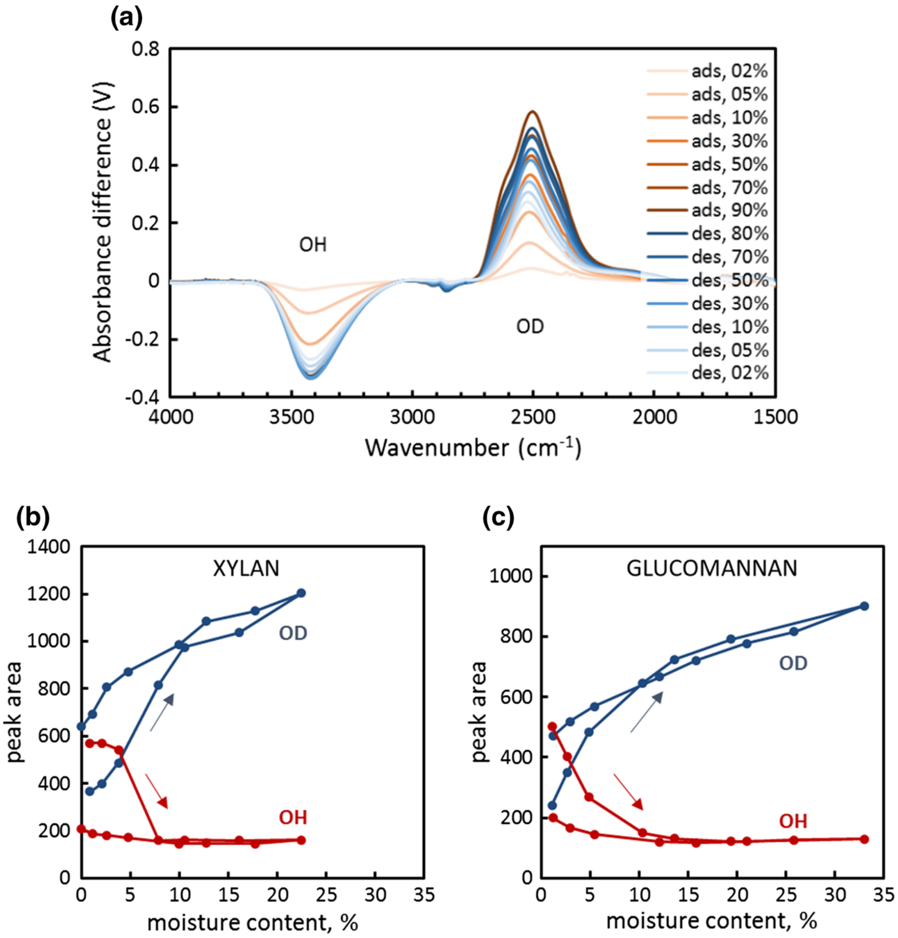


Fig. 5 FTIR spectral differences during sorption and desorption of D_2O for a glucomannan film **a** (the conditions given as %RH) and the evolution of OH and OD peak areas for **b** arabinoxylan and **c** glucomannan during adsorption and desorption of D_2O as a function of moisture content (% based on dry weight)

the difficulties of avoiding small traces of normal water in the surrounding laboratory environment as the system was not perfectly isolated from the environment allowing small quantities of H_2O to enter the system and becoming an important proportion of the nearly dry atmosphere. As evident for the dry conditions for both the glucomannan and the xylan there was a mismatch between the peak areas of the decrease in the OH peak with the increase of the peak areas of the OD peaks, the decrease in OH peak being larger than the corresponding increase in the OD peak. This fact relates to that the molecular absorptivity is lower by a factor of about 0.7 for D_2O as compared to H_2O for the corresponding absorption peaks of 2504 cm^{-1} and 3404 respectively (Venyaminov and Prendergast 1997; Max and Chapados 2009). For the xylan and glucomannan samples here measured a ratio between the decrease in OH absorbance and the increase in OD absorbance for dry conditions was calculated to be 0.75 in both cases.

For both xylan and glucomannan the substitution was not total, after the full D_2O adsorption–desorption cycle, the OH peaks did not decrease to zero. This means that some of the OH-groups were more resistant to hydrogen–deuterium exchange than most OH-groups. The amount of non-exchangeable sites can be estimated by comparing the OH peak areas at the maximum moisture (D_2O) content with that of the total OD and OH peak at dry conditions (taking into account the differences in absorptivity) in order not to take into account the contribution from moisture. This gives that the percentage of inaccessible sites for glucomannan is roughly $130/(200 + 470/0.75) = 15.7$ % and for xylan $161/(209 + 639/0.75) = 15.3$ % (Fig. 5b, c). As these hemicelluloses form homogeneous and amorphous films (Stevanic

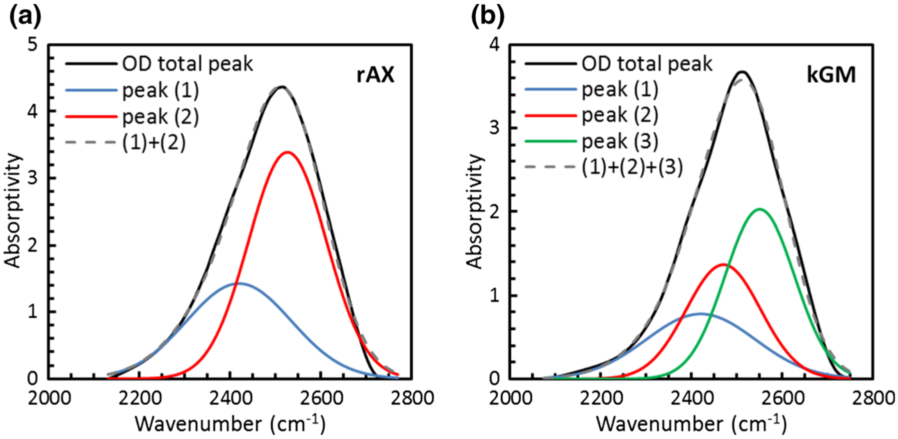


Fig. 6 An example of the decomposition of the OD absorbance peak of **a** xylan and **b** glucomannan into subpeaks at highest moisture content

et al. 2011) it is surprising that not all OH-groups were exchangeable. It could also be debated whether a phenomenon like hornification has any strict correlation to the possibility of OH–OD exchange as claimed by (Pönni et al. 2014) considering that not all OH groups in the studied amorphous hemicelluloses seems to be exchangeable. It should also be noted that some OH groups are very easily exchanged already in the very first drying process when the hemicelluloses were exposed to essentially zero humidity, the small amounts of heavy water still present in the circulating system rendered an exchange of about 20 % of the available OH-groups.

It is well known that both the OH and OD peaks are composed of a multitude of peaks associated to the different hydroxyl groups. Deconvolution has in many cases been applied to further examine the hydroxyl groups at play (Fengel 1993). For hexoses (glucose, mannose), three absorption peaks are to be expected while for pentoses (xylose, arabinose) two are expected. In Fig. 6 deconvolutions of the OH peak of the dry xylan and glucomannan are illustrated. The peak positions were calculated such that they minimized the error associated to the deconvolution. For cellulose, deuteration has been noted to shift the OH-bands by approximately 850 cm^{-1} to lower wavenumbers rendering a perfect match for all the three OH/OD-peaks (Nishiyama et al. 1999). Theoretically, based on the increased mass of deuterium compared to hydrogen, a shift factor of 1.34 for the OH-vibration/OD-vibrations has been computed (Jarvis and McCann 2000). As a compromise a shift to lower wave-numbers of 900 cm^{-1} was applied here.

When comparing the deconvoluted peaks it is evident that for xylan (Fig. 7a, b) the two peaks behaved similarly. Disregarding some baseline errors it seems as the two OH groups exchanged in about equal amounts to OD. A good agreement between the increase in the two OD-peak areas and the decrease of the corresponding OH-peak areas was also found. For the glucomannan the contribution from the different adsorption sites seems however not to be equal (Fig. 7c, d). In this case the lowest frequency peak (wavenumber 3450 cm^{-1}) appeared to be the most reactive. This peak is most commonly attributed to the intermolecular O(6)H–O(3) vibration (Agarwal et al. 2011; Marechal and Chanzy 2000). For cellulose the stability of the hydrogen bonds, based on molecular simulations (Agarwal et al. 2011; Bergenstråhle et al. 2007) as well as on FTIR monitored deuterium exchange (Hofstetter et al. 2006), has been found to be in the order $3450 > 3240 > 3350$ cm^{-1}. However, it may be assumed that for this noncrystalline glucomannan the accessibility towards the intermolecular O(6)H–O(3) bond (corresponding to wavenumber 3450 cm^{-1}) may be easier than towards the other intramolecular bindings. The agreement between the increase in the three OD peak areas (taken at 0 % RH) and the decrease of the corresponding OH-peak areas were also fairly good.

Conclusion

In order to better understand the interaction of moisture with the hemicelluloses in wood, model

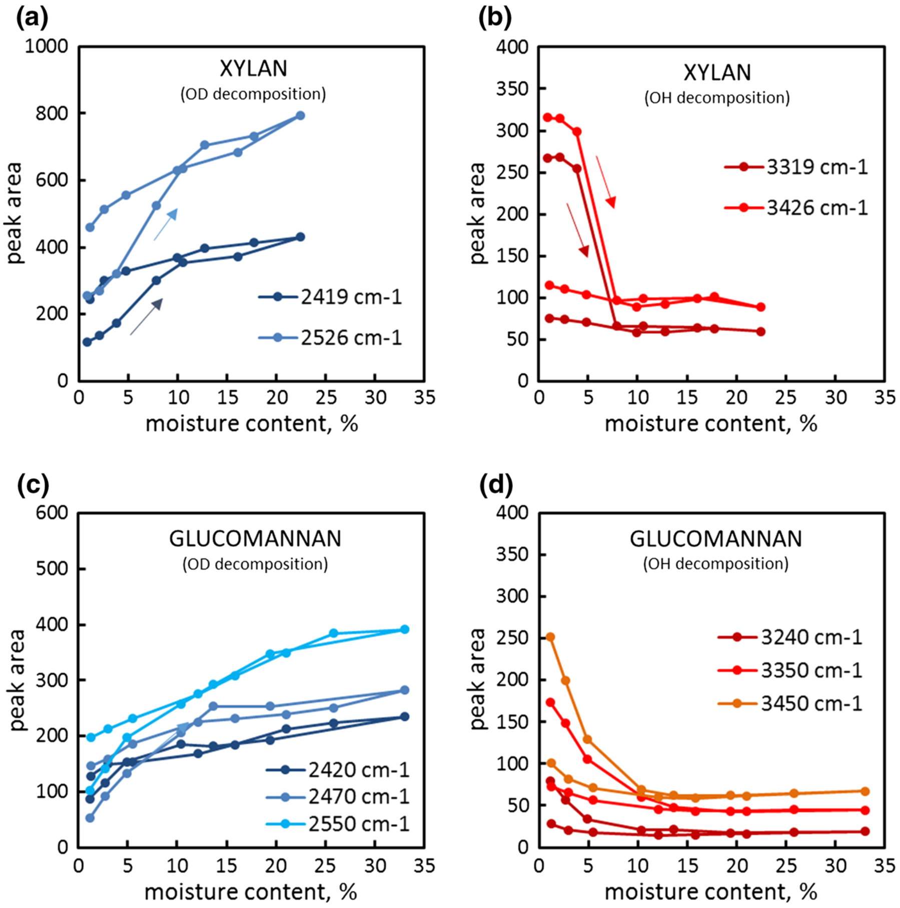


Fig. 7 Decomposition of hydroxyl peaks for arabinoxylan; **a** OH and **b** OD range and for glucomannan; **c** OH and **d** OD range, as a function of moisture content (% based on dry weight)

experiments of the sorption process of the two major types of hemicelluloses in wood, glucomannan and xylan, were examined. DMA measurements showed that both hemicelluloses behaved typically upon moisture adsorption: the increasing adsorbed water causes hygroscopic swelling approximately linear with moisture content and weakening of the solid structure observed as a decrease of modulus by more than 50 %. It was demonstrated through FTIR measurements that, although these polymers are fully amorphous, they do not seem to be totally moisture-compatible over the RH-range, leaving approximately 15 % of the OH-groups as non-exchangeable during deuteration. For the xylan the two hydroxyl groups seemed to be exchangeable to the same extent while for the glucomannan the peak most commonly associated to the O(6)H groups showed a much higher degree of exchange compared to the other two hydroxyls. In the sorption process, the exchange dynamics takes mainly place up to a moisture content of 10 % while further sorption of deuterium does not promote further exchange.

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