

MOISTURE IN UNTREATED, ACETYLATED, AND FURFURYLATED NORWAY SPRUCE STUDIED DURING DRYING USING TIME DOMAIN NMR¹

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Abstract. Using time domain NMR, the moisture in Norway spruce (*Picea abies* (L.) Karst.) sapwood subjected to four different treatments (never-dried, dried and remoistened, acetylated, and furfurylated) was studied during drying at 40°C, at sample average moisture contents above fiber saturation. Spin-spin relaxation time distributions were derived from CPMG relaxation curves using multiexponential fitting (CONTIN), and the resulting water populations were assigned according to the literature and their behavior during drying. It was found that both acetylation and furfurylation increased the average spin-spin relaxation time of the lumen water in earlywood tracheids from about 80–100 ms to 200 and 300 ms, respectively. The average spin-spin relaxation time of the cell wall water was reduced from about 1.4 to 0.65 ms by furfurylation, while acetylation had less effect on this water. The relaxation times of both the earlywood lumen water and of the cell wall water were slightly longer for the never-dried samples than for the dried and remoistened samples.

Keywords: Time domain NMR, spin-spin relaxation, wood, moisture, water, acetylation, furfurylation.

INTRODUCTION

Almost all engineering properties of wood are dependent on moisture content. Moisture affects dimensional stability, mechanical properties, and susceptibility toward biological degradation. Because of its paramount importance for construction purposes, moisture in wood has been studied for decades, but the basic understanding of how moisture is bound and transported within

solid wood during sorption and desorption is still not complete. With regard to different types of chemical modification aimed at reducing moisture uptake, an in-depth understanding of how and why they function is in some cases also lacking, thus preventing further development other than through 'trial and error.' In the present work, we explore the use of Time Domain ¹H Nuclear Magnetic Resonance (TD NMR) for the study of moisture in chemically modified wood during drying. For comparison, we also include two types of untreated wood: never-dried wood, and dried and remoistened wood.

Time domain ¹H nuclear magnetic resonance has been used extensively to study moisture in

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untreated wood. The majority of the studies have involved relaxation curves obtained using either the Free induction decay (FID) experiment, the Carr-Purcell-Meiboom-Gill (CPMG) experiment, or a combination of these. From the relaxation curves, spin-spin relaxation times, also called T_2 values may be obtained. Roughly speaking, FID may give information on both the solid wood and the moisture inside it, while CPMG solely reflects the moisture. While pioneering works focused on measuring moisture content by separating FID relaxation curves into a solid and a liquid component (Sharp et al 1978), later works using mainly CPMG relaxation have described the nature of the liquid component (Flibotte et al 1990; Araujo et al 1992, 1994). An analysis of the CPMG relaxation curves starts by a deconvolution of the curve into a number of components. This deconvolution is no simple task, and many models are able to describe the relaxation data equally well from a mathematical point of view (Whittall and MacKay 1989). While the accuracy of the mathematical fit of a relaxation curve is a prerequisite for obtaining knowledge about the states of water present, accuracy in itself does not mean that the deconvolution has any physical meaning. This implies that any assignment of water components in wood identified from a deconvolution of CPMGs should be considered with caution.

Water molecules diffuse (ie move) during the measurement, and if the cell diameters are so small that a substantial part of the water molecules collide with the cell walls during the time span of the measurement, the ^1H population in the water will exhibit a shorter relaxation time than in unconfined water, although being chemically identical. This phenomenon may be used to estimate cell sizes from relaxation curves of wood (Araujo et al 1993). However, a shortening of the relaxation time of hydrogen nuclei in water in wood compared with unconfined, liquid water may also be caused by the water molecules being sorbed to hydroxyl groups within the wood cell wall, such that both compartmentalisation and H-bonding result in a reduction in

the T_2 of ^1H in water within wood. A number of studies involving analysis and interpretation of relaxation curves from moist wood or other cellulosic materials have been published. Table 1 presents sets of assignments of spin-spin relaxation times for softwoods obtained from CPMG relaxation curves. Table 1 shows that above the fiber saturation point (FSP) the T_2 of water within the cell wall has been found to be around 1 ms, and to decrease to below half of that value below the FSP. Water in the lumens has been found to have T_2 values in the range from 2.2 to about 100 ms, depending on the cell radius. None of the studies seem to have been carried out on never-dried wood.

The purpose of the present work was to explore the use of TD NMR for the study of moisture in acetylated and furfurylated wood during drying as compared with untreated wood samples, including green wood. Acetylation and furfurylation are chemical modifications aimed at reducing the moisture uptake and protecting the wood from biological degradation. Earlier, acetylation was thought to reduce moisture uptake only through bonding of acetyl groups to hydroxyl groups in the cell wall, blocking their accessibility to water (Matsuda 1996). Recently, however this interpretation has been questioned by Papadopoulos and Hill (2003) and Hill et al (2005) who have proposed that bulking by the size of the adduct plays a more important role than the substitution of hydroxyl groups with regard to the reduction of water uptake. How furfurylation reduces moisture uptake is presently unknown. Unpublished work carried out at the University of Copenhagen indicates that a furfuryl alcohol (FA) polymer is formed within the cell wall, thus partially blocking the access of water.

MATERIALS AND METHODS

Samples

Cylindrically shaped sapwood samples of 14 mm dia were drilled from 10-mm-thick disks taken from a Norway spruce stem (*Picea abies*

TABLE 1. Literature values for softwood spin-spin relaxation times determined using CPMG experiments. MC: moisture content, FSP: fiber saturation point.

Reference	Material	T2 relaxation times (ms) identified and their assignments
Flibotte et al (1990), which includes data from Menon et al (1987)	Western red cedar (<i>Thuja plicata</i>) sapwood (MC: 28–221%), heartwood (MC: 8–35%), juvenile wood (MC: 9–30%)	Sapwood Bound water: 2–4 Water in latewood and ray lumens: 20–100 Water in earlywood lumens: 100–300 Heartwood and juvenile wood Bound water: 0.3–1 Non-volatile extractives or water in sealed compartments: ~50 (tentative assignment)
Araujo et al (1994)	White spruce (<i>Picea glauca</i>) Sapwood, heartwood and juvenile wood, various moisture contents.	Bound water: 1 Lumen water: 10–100 depending on radius
Araujo et al (1994)	Lodgepole pine heartwood (<i>Pinus contorta</i>), various moisture contents below and above the FSP up to saturated	Bound water: less than 0.2 below the FSP, increasing to about 1 above the FSP. Lumen water: above 2.2
Labbé et al (2002)	Maritime pine (<i>Pinus pinaster</i>) sapwood, 61% moisture	Dry cell wall: 0.003–0.007, 0.06–0.07 and 0.37–0.46 Bound water: 2.2–3.53 Lumen water in latewood lumens: 23.3–29.5 Lumen water in earlywood lumens: 75.9–96.2
Labbé et al (2006)	Maritime pine (<i>Pinus pinaster</i>), Above the FSP	Bound water: ~1 Lumen water: 3 populations in the range from 10 to 100.

(L.) Karst.). Processing of the stem took place within a few days after harvest, and care was taken throughout to prevent samples from drying out. After processing, the samples were packed in plastic with an excess of demineralized water. All samples were then subjected to neutron radiation (1×15 kGy) to prevent biological degradation during storage (mold fungi). As a further precaution samples were stored at $+5^\circ\text{C}$.

Four wood sample types were produced:

- *Never-dried samples (denoted N)* were stored in demineralized water at $+5^\circ\text{C}$. Before use the samples were put in a solution of sodium azide (NaN_3 , 200 mg/L) for 24 h to prevent biological degradation during the experiment.
- *Dried samples (denoted D)* were dried at 103°C and then vacuum saturated with demineralized water containing sodium azide (NaN_3 , 200 mg/L). The samples were saturated in the water for 2–3 h at 26–30 kPa followed by 24 h at atmospheric pressure.
- *Acetylated samples (denoted A)* were treated using a lab-scale set-up adapted from Rowell et al (1986). The samples were dried at 103°C . They were then subjected to vacuum drying for 18 h, after which enough acetic anhydride to cover all samples was added. After 1 h, the pressure was equilibrated, and the samples were boiled ($\sim 140^\circ\text{C}$) in acetic anhydride for 4 h. Finally the samples were dried at 103°C for about 24 h. The weight percent gain (WPG) was around 20%. After acetylation the samples were vacuum saturated in the same way as the dried samples (type D).
- *Furfurylated samples (denoted F)* were treated in a lab-scale set up. Untreated samples were predried at 103°C for 16 h and impregnated in an autoclave (full vacuum for 30 min followed by a pressure of 1.2 MPa for 120 min). Excess liquid was wiped off, and the solvent was partly evaporated in an oven using a tem-

perature ramp from 20 to 40°C during 4 h. Thereafter the samples were wrapped in aluminium foil and cured for 16 h at 103°C. The foil was removed, and the samples were dried for 7 h at 103°C to evaporate condensed water and unreacted monomer. The impregnation fluid consisted of furfuryl alcohol (55 wt-%), ethanol (39 wt-%), citric acid (catalyst, 2 wt-%), and de-ionized water (4 wt-%). The average WPG was 63%, indicating that the impregnation was successful even though the samples were made from spruce. This is most likely due to the small sample size used.

For the acetylated and furfurylated, it is possible that unreacted chemicals were still present in the wood samples after the modification. However, for the acetylated samples it is not likely that acetic anhydride remained unreacted both during impregnation and the subsequent water saturation, as it is a very reactive substance, especially with water. For the furfurylated samples, it is not unthinkable that unreacted furfuryl alcohol remained in the samples.

In addition to the wood samples, a sample of double-distilled furfuryl alcohol with citric acid added (30 mM) was measured directly after mixing, and after 24 h of curing at 130°C, at which time solid poly(FA) had formed.

Time Domain ^1H NMR

Time Domain ^1H NMR analyses were done using a Bruker mq20-Minispec, with a 0.7 Tesla permanent magnet (20 MHz proton resonance frequency), operating at 40°C. The transverse (T_2) relaxation times were determined using the Carr-Purcell-Meiboom-Gill (CPMG) sequence. 7500 echoes were collected with a pulse separation of 0.05 ms, the acquisition of 32 scans and a 5-s recycle delay. The Laplacian transformation method CONTIN, as described by Provencher (1982) was used to determine relaxation time distributions.

Four samples of each type were put in glass NMR tubes (18 mm dia), and three tubes were prepared for each of four sample types. Each

tube was measured four times: fully saturated, and after 60, 120, and 180 min of drying at 40°C. In addition, three furfurylated samples were measured after drying for 24 h at 100°C. The relaxation time distributions reported are means of three distributions found for each combination of sample type and drying time. The samples were not measured while in equilibrium with the ambient conditions, and the CPMGs consequently are snapshots of the moisture present in the samples at certain points during drying, rather than reflecting equilibrium conditions corresponding to specific relative humidity levels. This implies that during measurements, moisture gradients were present within the samples, and that even though the dry basis moisture contents determined were above the FSP for all measurements, regions at or near the sample surfaces may have been below the FSP. Given the bulk nature of the NMR measurement, however, the presence of any moisture gradients is not a factor in these experiments.

The same gain setting was used for all measurements on wood samples except for the oven-dried furfurylated samples for which a higher gain was used, due to the much lower moisture content of these samples. The current work is focused on changes in the relaxation times and their distributions, indicative of alterations in both cell wall chemistry and compartmentalization, as a function of treatment and moisture content. Peak area comparisons are reported only within a sample type.

Partial Least Squares (PLS) Modeling

To further elucidate which parts of the T_2 distributions that were most closely related to the moisture content and the nature of any relationship, a Partial Least Squares (PLS) regression model was developed between T_2 distributions and moisture contents. The purpose of the model was to explore this relationship for the samples included in the data set of the present study, rather than to develop a generally applicable tool for the prediction of moisture contents from T_2 distributions. Therefore, all samples were in-

cluded in the calibration step, no validation was performed, and consequently the number of factors was not optimized.

RESULTS

Overview of T_2 Distributions

An overview of the data from the wood samples is given in Figs 1 and 2, which show the T_2 distributions for all four sample types (never-dried, dried and remoistened, acetylated, and furfurylated) at four different times during drying. Large differences in moisture contents between the four sample types are seen, but no

samples reach average moisture contents below the fiber saturation point (about 30% for untreated wood, the same or lower for modified wood). The figures also show that the T_2 distributions have a few traits in common. For the saturated samples, a major peak within the range from 80 to 300 ms is present for all four samples (this peak is hereafter denoted peak II). The area of this peak becomes smaller as the sample dries, indicative of a water population that evaporates from the samples during drying. According to Table 1, this population should be free lumen water in cells with relatively large lumens such as earlywood tracheids. The peak

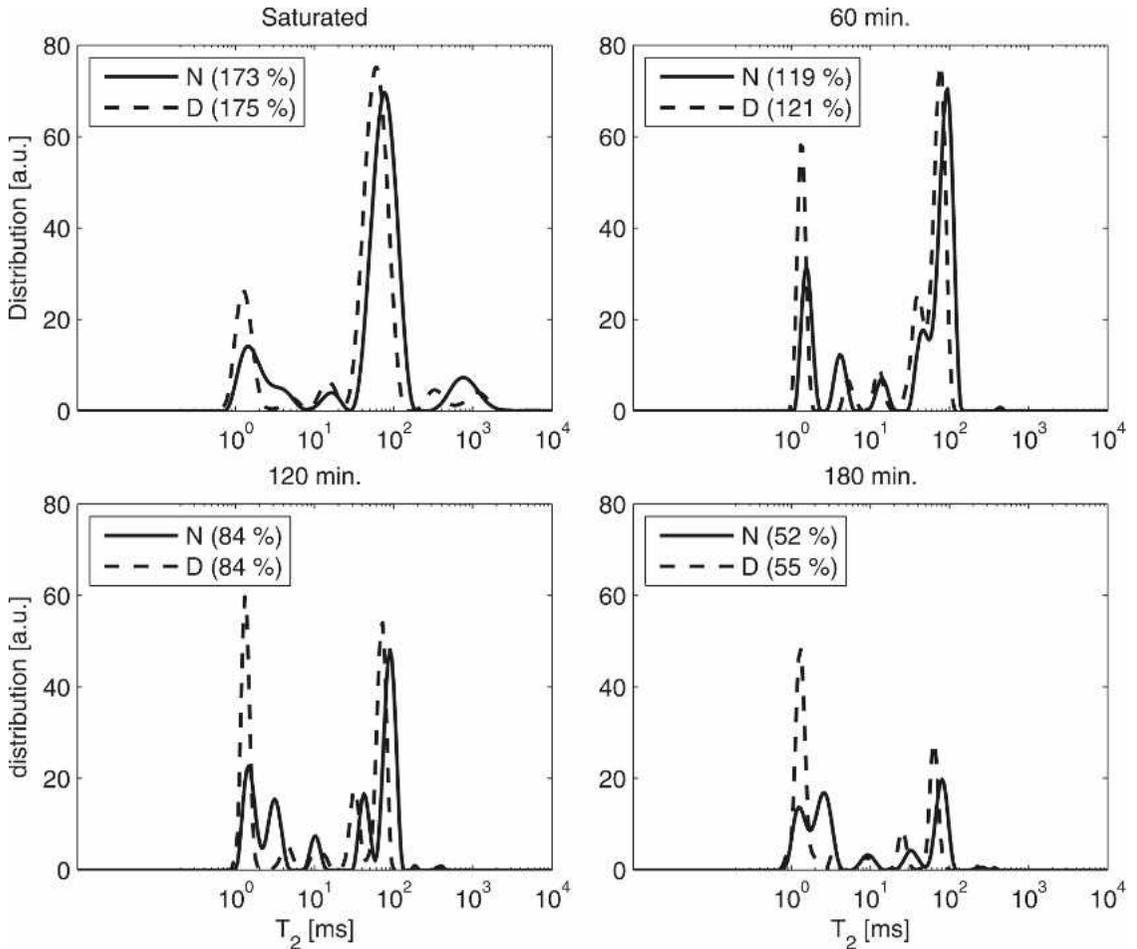


FIGURE 1. T_2 distributions of never-dried (N) and dried and remoistened (D) samples measured fully saturated and at three different times during drying.

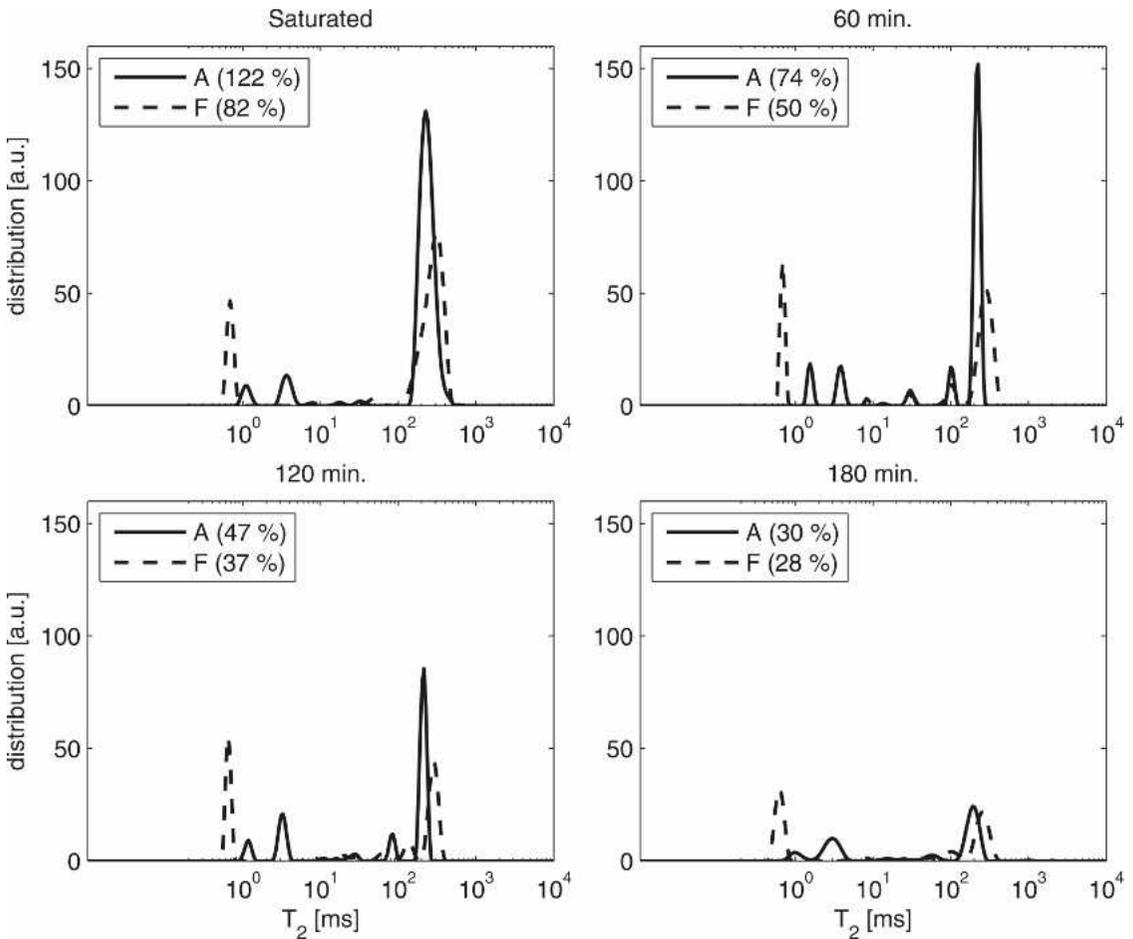


FIGURE 2. T_2 distributions of acetylated (A) and furfurylated (F) samples measured fully saturated and at three different times during drying.

for the shortest T_2 found in the samples at around or below 1 ms initially appears to become narrower and higher, and then it slowly decreases (this peak is hereafter denoted peak I). According to Table 1, this water population should be due to bound or cell wall water. The peaks found between these two peaks do not appear to change systematically during drying for any of the sample types, and they will not be discussed in this work. According to Table 1, these intermediate populations could be due to lumen water in cells with relatively small lumens such as those of latewood tracheids or ray cells, but water inside larger voids inside the cells walls (cracks etc.) is another possibility.

The T_2 distributions in this work are consistent with those reported by Araujo et al (1992).

The distributions for the never-dried and for the dried and remoistened types (N and D, Fig 1) appear to be rather similar, but with a few exceptions. For all four times, peak II is located at slightly longer times for the never-dried than for the dried and remoistened samples. For the never-dried, peak I is a double peak that is not base-line separated (except for the measurement after 60 min), while the dried and remoistened show only one high and narrow peak at the position of one of these peaks (the one for the shortest T_2).

The acetylated samples also have two peaks in the lower end of the distribution, while the furfurylated samples have one, like the dried and remoistened samples. Figure 3 shows peak positions and peak areas for peaks I and II. As noted in the 'Materials and Methods' section, peak areas or heights are compared only between different measurements on the same sample type, not between different sample types. The position of peak I of the furfurylated sample is only about one-half the time of the positions of the two unmodified sample types (N and D), ie 0.65 ms compared with about 1.4 ms. For the acetylated samples, peak I is positioned at a little shorter times than for the N and D type samples, except for the distribution recorded after 60 min, for which the position is at a longer time than

that of the N and D type samples. The area of peak I is seen to increase a little during the first 60 min of drying, except for the furfurylated samples. As also seen from Figs 1 and 2, the position of peak II of the modified samples (A and F) is at markedly longer time than the positions of the unmodified samples (N and D), also for similar moisture contents. The area of peak II decreases throughout the drying for all four sample types.

Exploratory PLS Modeling of Moisture Content

The results from the modeling are shown in Fig 4. Figure 4a shows the actual moisture contents vs the moisture contents predicted from a two-

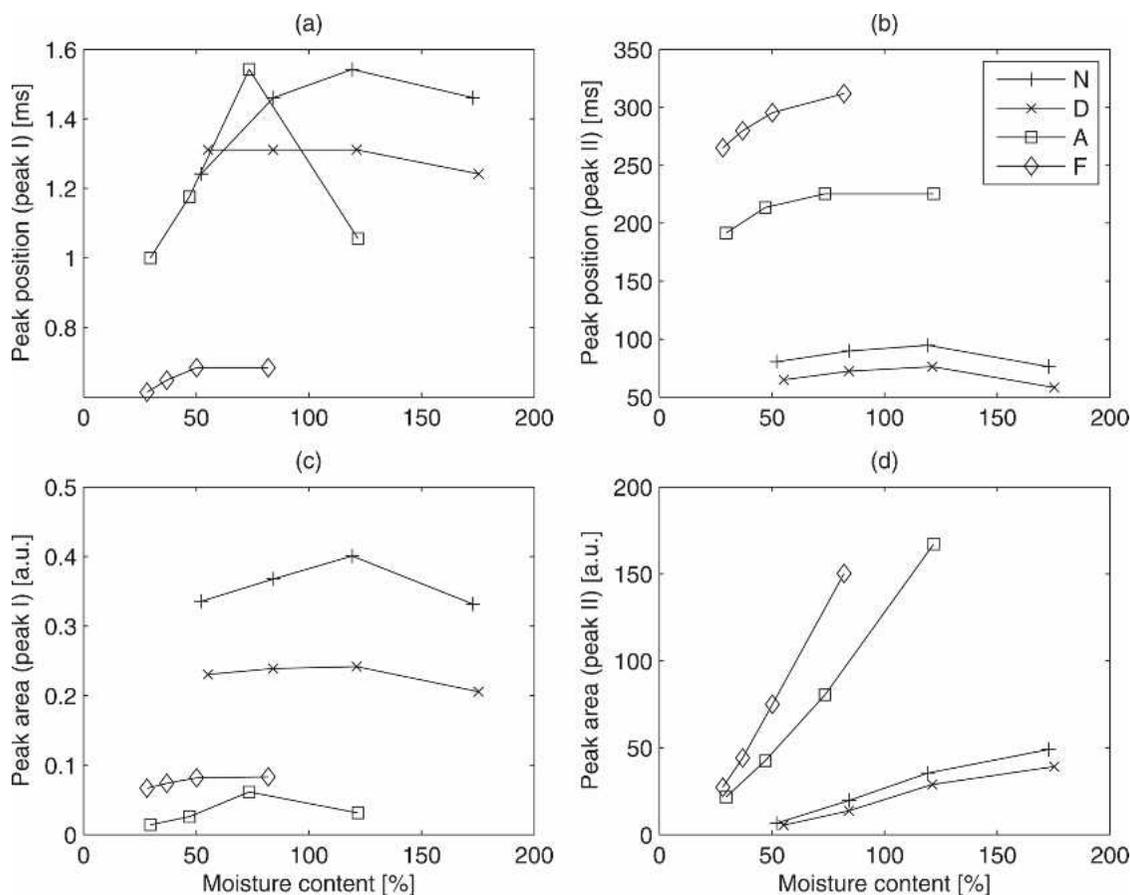


FIGURE 3. Positions and areas of the cell wall water T_2 peak (peak I) and of the earlywood tracheid lumen water peak (peak II) vs moisture content. The legend in (b) applies to all four subplots.

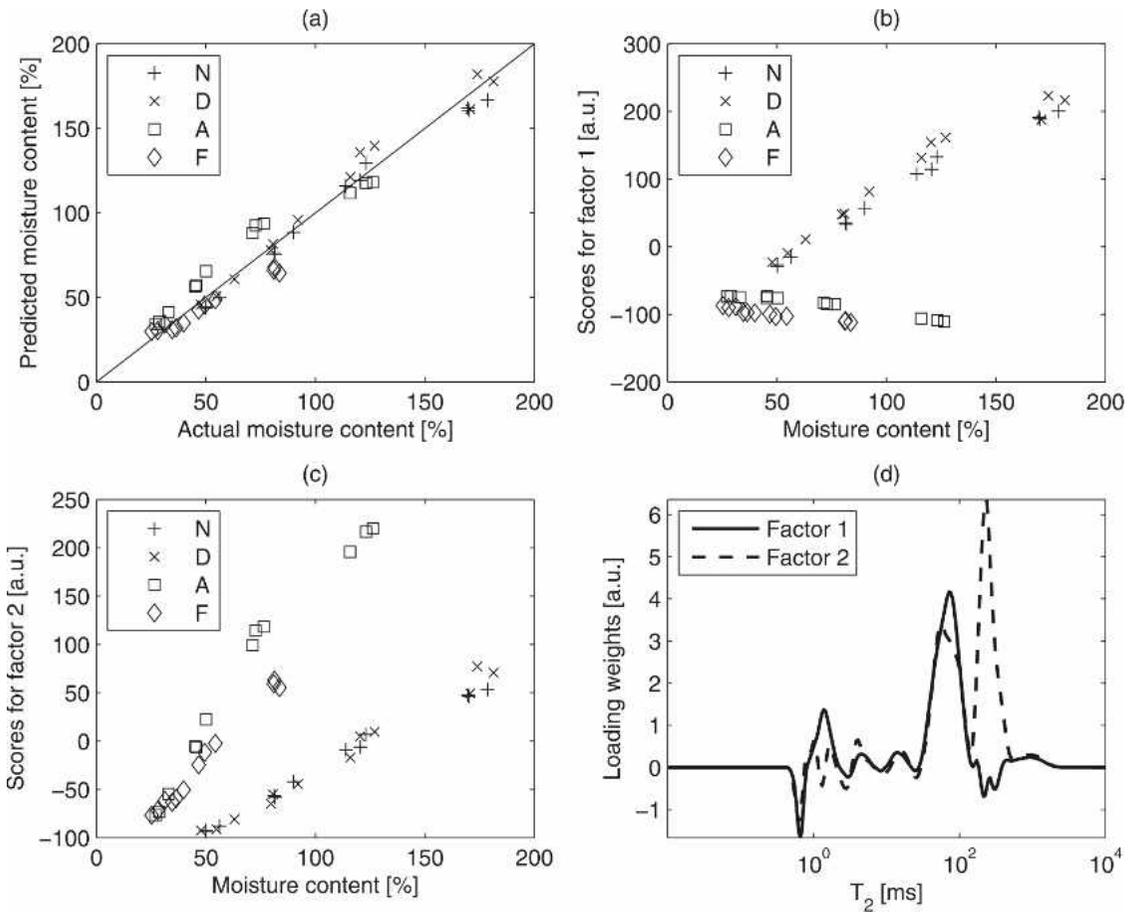


FIGURE 4. 2-factor PLS modeling of moisture content from T_2 distributions. The root mean square error of calibration of the model was 8.93% moisture, and the coefficient of correlation between actual and predicted values was 98.1%. The modeling showed that the 80–100 ms peak in untreated samples (N and D) and the 200–300 ms peak in the modified samples (A and F) are related to similar pools of water.

factor PLS model. The prediction is good enough for the current purpose for all four sample types, and consequently no more factors were included in the model. Figures 4b and 4c show the relationship between moisture contents and the scores of the two factors. Figure 4b shows that factor 1 is related to the moisture contents of only the N and D type samples, while factor 2 is related to the moisture contents of all four sample types, but with a systematic difference between unmodified (N and D) and modified (A and F) samples. Figure 4d shows the loading weights of the two factors. Scores for factor one are positively related to peak II of the N and D type samples at 80–100 ms, while

scores for factor 2 are positively related to both this peak and to peak II of the A and F type samples at 200–300 ms. This agrees with the scores in Figs 4b and 4c. Both factors have negative loading weights for peak I at approximately 1 ms, which agrees with the observation that for three of the four samples types (all except type F) this peak increases during the first hour of drying where most moisture is lost. The middle peaks appear to be positively correlated to moisture content, but this is not easily confirmed from Figs 1 and 2. The result that the 80–100 ms peak of the N and D type samples and the 200–300 ms peak of the A and F type samples behave similarly in the model, and even are included in

the same PLS factor (factor 2) shows that despite the difference in T_2 , both these peaks are due to lumen water that evaporated during drying.

T_2 Distributions from poly(FA) and from Oven-dried F Type Samples

Figure 5 shows the T_2 distributions for the furfuryl alcohol+citric acid (FACA) sample before and after curing, and for furfurylated wood before and after oven-drying. The figure shows that the ^1H populations in furfuryl alcohol have longer relaxation times than those of lumen water in wood. This probably has to do with the lack of compartmentalization in the furfuryl alcohol. Curiously, two distinct populations appear to be present, one at ~ 1275 ms and one at ~ 2445 ms, perhaps ^1H nuclei involved in C-H bonding and O-H bonding, respectively. After curing, these signals have disappeared and only signals in the range from 0.1 to 4 ms are left. This is in the same region as peak I of the furfurylated samples before and during drying at 40°C (at approximately 0.65 ms, see Fig 3a). Thus, in theory this peak could be due to poly(FA) within the wood cell wall. However,

the peak at 0.65 ms disappears from the furfurylated wood after the more severe oven-drying, which is a strong indication that this peak is due to water within the cell wall.

DISCUSSION

The most dominant difference between the modified and unmodified wood samples was that both acetylation and furfurylation had a large and similar effect on the dominant peak corresponding to water in earlywood tracheid lumens. Both treatments move the position of this peak from about 80–100 ms to 200–300 ms (Fig 4b). The PLS modeling showed that this water gradually disappeared from all samples, so it is reasonable to consider this population to be earlywood tracheid lumen water in all four sample types, despite the differences in relaxation time. That both acetylation and furfurylation increase the T_2 of the earlywood lumen water shows that neither treatment fills the lumens or reduces their diameter (which would move the position of this peak downward). A possible explanation could be that the inner diameter of the cells increased as a result of the modification (A or F), thus increasing the average diffusion length of the lumen water. However, swelling does not normally affect the lumen diameters of wood cells, and also this explanation would explain differences seen only as long as the lumens were filled with water, not the differences seen during drying. A more likely explanation to the shift in peak position is that the A and F treatments make the wood cell walls more hydrophobic, and that the water in the lumens consequently becomes freer, similar to the effect of charring reported by Elder et al (2006). In the present case, one can imagine that the effect has to do with the contact angle of the water on the inside walls of cells during drying above fiber saturation, where the lumens are gradually being emptied of liquid water. If the lumen water in N and D type samples has a contact angle close to 0° , then the diffusion length during an NMR measurement, and thereby the T_2 of the water within this water film, would unlikely be affected by moisture content, since the moisture

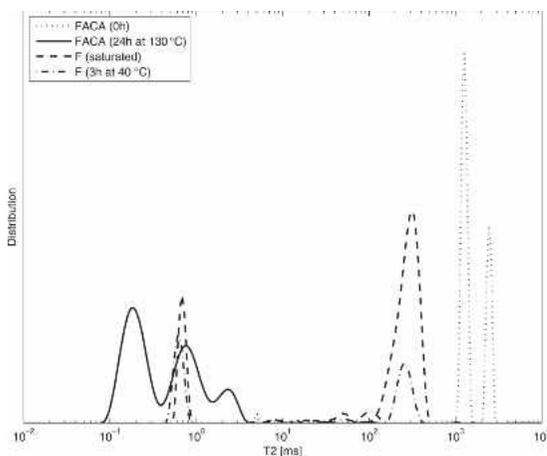


FIGURE 5. T_2 distribution curves for furfurylated samples before and after drying at 103°C and for furfuryl alcohol before and after curing at 130°C . The curves have been scaled individually to allow easy comparison of peak positions. The figure indicates that the 0.7 ms peak (peak I) of the furfurylated samples (Fig 2) most likely was due to water and not furfuryl alcohol or poly(FA).

content under these circumstances can be expected to influence the extent rather than the thickness of the film of water on the lumen side of the cell walls. For A and F type samples, the situation could be the opposite, if the contact angle is high. Then in the extreme case, droplets of water and not a film would form on the lumen side of the cell walls, and the radius of these droplets would decrease during drying above fiber saturation, thus decreasing the diffusion length, and thereby the T_2 . In Fig 3b it is seen that the position of peak II decreases during drying for the modified samples, while the position is more or less constant for the unmodified samples, in accordance with the proposed description. The difference between acetylated and furfurylated wood could be due to the difference in WPG, as the furfurylated samples were much more heavily treated, and their cell wall surfaces therefore presumably more hydrophobic.

The changes in the cell wall water that peak at around 1 ms following wood modification are more difficult to interpret. Assuming that the 0.65 ms peak seen for the F type samples actually is due to cell wall water, as suggested by Fig 5, then the peak position is shifted toward shorter times for these samples, while the effect appears to be smaller and less clear for acetylation. For untreated wood, water within the cell wall is thought to be present as clusters of water molecules or single molecules that are hydrogen bonded to sorption sites, mainly hydroxyl groups (Hartley et al 1992; Berthold et al 1996; Salmén 1997). If the cell wall is bulked by chemical modification, it is reasonable to assume that the spaces available for water are greatly reduced. At the microscale inside the wood cell wall, the concepts of hydrophobic/hydrophilic surfaces and contact angles do not apply. The most dominant factor with regard to T_2 relaxation of the cell wall water is probably how free the individual water molecules are to move, with confined spaces and 'frozen' positions leading to shorter relaxation times. The bulking of the cell wall in modified wood may thus at the same time cause the cell wall water to relax faster and the lumen water to relax more

slowly. The fact that the WPG was much higher for furfurylated than for acetylated wood could explain the difference seen between these two treatments, but the difference could also arise from the chemistry of the modification.

It is difficult to understand the initial increase in the area of the cell wall water peak seen for all except the furfurylated samples. An increase in the amount of water inside the cell wall during the initial phase of drying compared with the fully saturated case appears unlikely. At present we can offer no explanation for this observation.

In comparing the N and D type samples (moisture contents given in Figure 1), it appears that the D type samples contain a little more water than the N type samples throughout the drying experiment. The difference is not significant (results not shown), but nevertheless appears to be systematic, and is in agreement with unpublished results for the same sample set. Defo et al. (1999) also found that green wood contained less water than dried and re-saturated wood, but in their case it was in equilibrium states at relative humidities above 99.3% (i.e. at water potentials above $-1000 \text{ J} \cdot \text{kg}^{-1}$). Drying is supposed to be an irreversible process making a percentage of the sorption sites within the wood cell wall inaccessible (hornification), which would imply that dried and remoistened wood should contain less water than green wood. For all measurements except one, the positions of both the cell wall water peak (peak I, Figure 3a) and the tracheid lumen water peak (peak II, Figure 3b) are lower for dried than for never-dried samples, in agreement with the theory of drying leading to hornification. It could be that moisture is transported out of hornified wood at a lower rate, and that the slightly higher moisture content in the dried and remoistened samples simply reflects a reduced outflux of water vapor during drying, since the samples were measured at certain fixed times during drying, and not in equilibrium states. Another and perhaps more likely explanation to the higher moisture contents found in the dried and remoistened wood could be that the vacuum saturation provided access to more sorption sites within the wood

cell wall. It should be emphasized, however, that the tendency seen was not significant for the subset of samples used in this work.

CONCLUSIONS

The water in never-dried, dried, acetylated, and furfurylated spruce sapwood was studied above fiber saturation. The CPMG relaxation curve was obtained for each sample in the fully saturated state, and three times during drying at 40°C.

The study showed that all four sample types had T_2 distributions that were systematically different from those of the other three types. Systematic differences were found in the two ^1H populations assigned to lumen water in earlywood tracheids and to water in the cell wall. Both of these peaks are placed at slightly higher times for the never-dried samples than for those dried and remoistened. Chemical modification of the wood affected both peaks markedly. Both acetylation and furfurylation increased the relaxation time of the lumen water from approximately 80–100 to 200–300 ms. This change was suggested to be a result of the cell walls becoming hydrophobic as a consequence of the wood modification. Furfurylation reduced the relaxation time of the cell wall water from about 1.4 to 0.65 ms. Acetylation also seemed to reduce the relaxation time of the cell wall water somewhat, but not as much or as clearly as furfurylation. It is suggested that the reduction in relaxation time was from a reduction in the sizes of the spaces available to water within the cell wall as a result of the cell wall bulking.

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