MOISTURE IN UNTREATED, ACETYLATED, AND FURFURYLATED NORWAY SPRUCE MONITORED DURING DRYING BELOW FIBER SATURATION USING TIME DOMAIN NMR[1]

Lisbeth G. Thygesen

Senior Researcher
Danish Centre for Forest, Landscape and Planning
University of Copenhagen
Rolighedsvej 23
DK-1958 Frederiksberg C, Denmark

*Thomas Elder**†*

Research Forest Products Technologist
Utilization of Southern Forest Products
USDA-Forest Service
Southern Research Station
2500 Shreveport Highway
Pineville, LA 71360

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Abstract. Using time domain–nuclear magnetic resonance spectroscopy, the moisture content (MC) in Norway spruce [*Picea abies (L.) Karst.*] sapwood, subjected to three different treatments (untreated, acetylated, and furfurylated), was studied during drying at 40°C at MCs below fiber saturation. Spin–spin relaxation time distributions were derived from Carr-Purcell-Meiboom-Gill relaxation curves using mulitexponential fitting (CONTIN). After conditioning for 6 wk at 100% RH, the modified wood samples had a MC of about 15%, whereas the MC of the untreated samples was about 30%. Two water populations with different relaxation times were found in all three sample types at this point: 1.1 ms and 0.15 ms (untreated), 0.5 ms and 0.15 ms (furfurylated), and 1.2 – 3.5 ms and 0.1 ms (acetylated). As the MC decreased, the relaxation time of the most slowly relaxing population decreased, whereas it remained more or less constant for the other population. For both the untreated and the furfurylated samples, the two populations merged at 5 – 10% MC, and relaxation times were identical for the two treatments at low MC. The two populations did not merge for the acetylated samples. These results indicate that while acetylation changed the interaction between water and the wood cell wall, furfurylation seemed to mostly affect the amount of water present within the cell wall at the beginning of the drying experiment.

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

INTRODUCTION

In a previous paper (Thygesen and Elder 2008), the nature of water in wood, modified by furfurylation and acetylation, was studied at moisture contents above the FSP using low field–time domain–nuclear magnetic resonance spectroscopy(LF-TD-NMR). The current article continues this work through an examination of modified wood as it is dried below the FSP. This will provide information about the behavior of water in the cell wall of modified wood at moisture contents (MCs) that are likely to occur during the service life of such wood.

LF-TD-NMR and its application to wood has been described in some detail previously (Elder et al 2006; Thygesen and Elder 2008) such that this introduction will be brief, and interested readers are referred to the cited articles and references. As the name implies, this technique uses a low magnetic field strength

* Corresponding author: telder@fs.fed.us
† SWST member
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(approximately 20 MHz proton resonance frequency), and as such, transformation into the frequency domain results in limited information. Magnetization decay can, however, provide information on molecular mobility expressed as spin–spin (or T_2) relaxation times. Studies of water in wood are typically based on the determination of T_2 using the Carr-Purcell-Meiboom-Gill pulse sequence (Flibotte et al 1990; Araujo et al 1992, 1994). Once the decay curve has been obtained, T_2 can be extracted as discrete values by fitting exponential functions or as distributions using linear and nonlinear methods (Provencher 1982; Whittall and MacKay 1989). T_2 values that have been reported for water in wood are 100 – 300 ms for free water in earlywood lumens, 20 – 100 ms for free water in latewood lumens (Flibotte et al 1990), and 0.2 – 3 ms for bound water (Araujo et al 1994; Labbé et al 2002). Changes in these relaxation times have been interpreted as reflective of chemical and physical modifications to wood that occur during processing.

The chemistry of modification and properties of modified woods have been reviewed by Matsuda (1996) and Rowell (2005). Recent work on furfurylation by the action of furfuryl alcohol has been concerned with spectroscopic determination of loading (Celen et al 2008; Venås and Rinnan 2008) and property enhancement (Lande et al 2008). In the latter work, it was found that at high levels of furfurylation, the hardness of the material, modulus of elasticity, modulus of rupture, dimensional stability, and resistance to biological and chemical degradation increase. The acetylation of wood has been an area of active research for a number of years and the technology was recently reviewed by Rowell (2006). In the recent literature, modification in general and acetylation in particular have been reported for homogeneous systems based on the dissolution of thermomechanical pulp fibers in ionic liquids (Xie et al 2007). High degrees of substitution are reported in the ionic liquid system along with changes in thermal properties and microscopic structure.

In the previous work (Thygesen and Elder 2008) with samples above fiber saturation, it was found that chemical modification of the wood altered the relaxation time distributions and increased the T_2 of water assigned to the lumens from 80 – 100 ms for the untreated controls to 200 – 300 ms. These data indicate an increasing level of hydrophobicity with modification. Conversely, the relaxation time of water in the cell walls was reduced with furfurylation, interpreted as a reduction in the size of pores from bulking of the cell wall, whereas acetylation did not have any systematic effect on this water.

MATERIAL AND METHODS

Norway spruce [*Picea abies* (L.) Karst.] samples were treated as previously described (Thygesen and Elder 2008), except never-dried samples were not included. The sample set thus included untreated, acetylated, and furfurylated wood. The average weight gain was 20% for the acetylated and 63% for the furfurylated samples. Samples in triplicate were conditioned in a dessicator over deionized water at room temperature for approximately 6 wk to reach a MC approaching fiber saturation. The samples were weighed and then dried in an oven at 40°C in 15-min intervals for up to 345 min. After each 15-min drying step, the samples were weighed and LF-TD-NMR spectra were recorded. The NMR spectra were recorded using a Bruker mq20-Minispec with a 0.7 Tesla permanent magnet (20 MHz proton resonance frequency) operating at 40°C. The NMR experiments determined spin–spin (T_2) relaxation times using the Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence with a pulse separation of 0.04 ms, the collection of 256 echoes, 32 scans, and a recycle delay of 5 s. Relaxation time distributions were calculated by performing an inverse Laplace transform on the CPMG results using the CONTIN algorithm described by Provencher (1982). Finally, the samples were oven-dried and dry-basis MC were determined at each time increment.

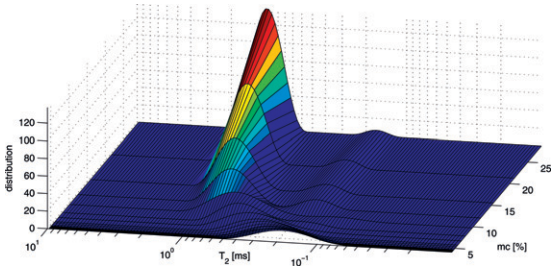

Figure 1. T_2 distributions during drying for an untreated Norway spruce sapwood sample.

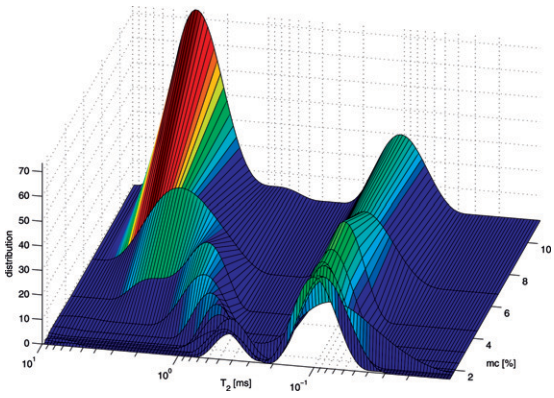

Figure 2. T_2 distributions during drying for an acetylated Norway spruce sapwood sample.

RESULTS AND DISCUSSION

T_2 relaxation time distributions and MC during drying are shown in Fig 1 (untreated), Fig 2 (acetylated), and Fig 3 (furfurylated) for one sample of each type. The figures show that after 6 wk at 100% RH, the MC was much lower in the chemically modified samples than in the untreated sample (about 15% compared with about 30%). This is as expected given the purpose of the modifications is to protect the wood from moisture uptake and biological degradation.

All three samples initially showed similar T_2 relaxation time distributions with a major peak in the 0.5 – 3 ms range and a minor one at about 0.1 ms. These values are both in the range of T_2 values found earlier for cell wall water in wood (Thygesen and Elder 2008 and references therein). All three samples show a gradual decrease

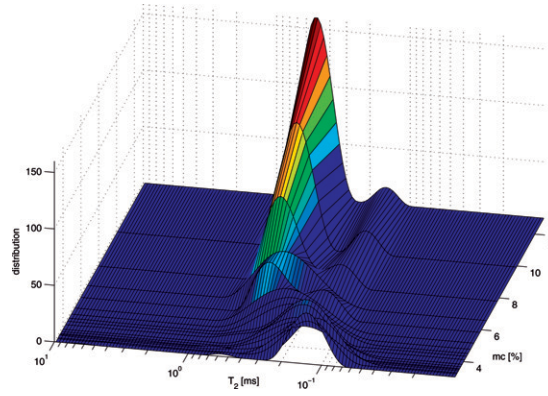

Figure 3. T_2 distributions during drying for a furfurylated Norway spruce sapwood sample.

in peak amplitude for the approximately 1 ms peak, but there are also differences as the samples lose moisture. For the untreated sample, the population corresponding to the lowest T_2 almost disappears at approximately 10% MC and at the same time merges with the more slowly relaxing population. For the furfurylated sample, the two populations start to merge at approximately 7% MC. For the acetylated sample, the two populations continue to be baseline-separated throughout the drying experiment.

Figure 4 shows T_2 peak positions vs MC for each of the 3 $\times$ 3 samples. The figure shows that for all treatments, the relaxation time for the slower relaxing component decreases with MC. Within the MC range for which data are available for all three sample types, the rate of this decrease is about the same for the furfurylated samples and the untreated controls but higher for the acetylated samples, indicating that the rate is not only dependent on MC, but is also influenced by the sample treatment. The T_2 for the faster relaxing population remains relatively constant for all three treatments with the untreated and furfurylated samples exhibiting similar relaxation times for this component, whereas those of the acetylated samples are markedly shorter.

From Fig 4, the MC at which the two populations merge appears to be somewhat higher for the untreated samples (about 10%) than for the

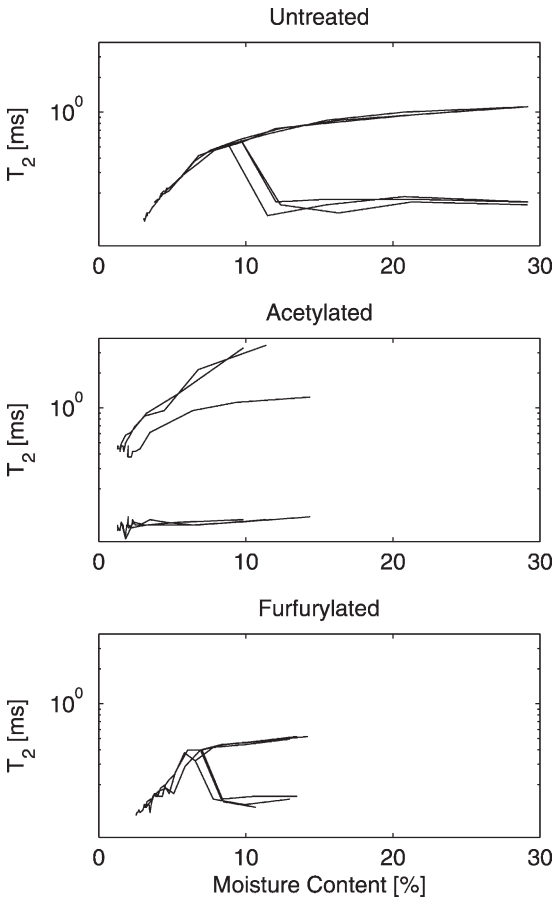

Figure 4. Peak positions from T_2 distributions vs MC. The figure shows data for all three samples per treatment (untreated, acetylated, and furfurylated), ie nine samples in total. Depending on the sample type and the MC, peak positions of 1 – 2 peaks per sample are shown.

furfurylated samples (about 7%). However, in Fig 4, the two peaks merge at the MC where they are no longer baseline separated, but as can be seen in Figs 1 and 3, the two populations are also discernable for lower MC (down to about 5% MC for both sample types), ie the transition from two to one population is gradual and not abrupt, and although the merging starts at different MC (at about 10 and 7%), it is complete at approximately the same MC for both treatments (at about 5%).

In a study of MC below the FSP in three different hardwoods, Almeida et al (2007) found only one component corresponding to cell wall water. The T_2 of this component decreased from 1 – 1.5 ms at fiber saturation to approximately 0.4 ms at about 7% MC. This is consistent with the results found for the major peak in the T_2 distributions for all three of the treatments of the present samples. Because the wood cell wall polymers have relaxation times in the tens of microseconds range (Menon et al 1987; Hartley et al 1994), the minor peak found in the present study most likely does not reflect solid wood cell wall material, although both its relaxation time and amplitude are mostly unaffected by MC. Rather, this peak reflects water that is more tightly bound than the main part of the cell wall water.

In the previous study of the same sample types, but above fiber saturation, only one peak assigned to cell wall water was found. This indicates that when lumen water is present and the cell wall is saturated, the signal from the cell wall water is not resolved into the two separate populations that may be identified in samples with lower MC. In that study, for MC in the 50 – 100% range, the T_2 relaxation time of the cell wall water was found to be approximately 1.4 ms for untreated wood and 0.65 ms for furfurylated wood, whereas acetylation did not seem to have any systematic effect on the relaxation time of the cell wall water. Because the two populations found in acetylated wood in the present study were found to be, respectively, more slowly and faster relaxing than the two corresponding populations in untreated wood, it is perhaps understandable that an average relaxation time comprising both of these populations does not differ systematically from the untreated wood. Regarding the furfurylated samples, it is possible that the slight difference between the furfurylated samples and the untreated samples seen in the present study for MC approaching fiber saturation is more marked above fiber saturation.

Figures 1 – 4 show that the cell wall water in the acetylated samples is clearly different from the untreated samples; the slow component relaxes more slowly than the corresponding one for the

untreated samples, whereas the fast component relaxes more rapidly than the corresponding component of the untreated samples. This is in contrast to the cell wall moisture in the furfurylated samples for which relaxation times are quite similar to those of the untreated samples. From Fig 4 it can be seen that the populations with shorter relaxation times are very similar, whereas the more slowly relaxing component of the furfurylated sample is slightly lower than for the untreated wood for the same MC in the 7 – 15% MC range. These differing results between the two wood modifications are highly interesting and potentially important. Acetylation, which truly modifies the woody cell wall, causes substantial changes in the relaxation time of cell wall water. Such changes in relaxation times are not, however, observed after furfurylation.

Furfurylation, although definitely involving the formation of a poly-furfuryl alcohol polymer inside the wood cell wall, does not appear to crosspolymerize with lignin in wood through covalent bonding to any significant extent (Venås et al 2006; Barsberg and Thygesen 2007; Venås 2008), although such bonds have been found to form in vitro between furfuryl alcohol and lignin model substances (Nordstierna et al 2008). There are no literature reports indicating chemical interactions of furfuryl alcohol with the polysaccharides in wood. However, furfuryl alcohol is highly polar, and such interactions are likely to occur during the impregnation phase. Conversely, the fufuryl alcohol polymer is hydrophobic, and substantial hydrogen bonding to carbohydrates after curing is more difficult to envision. Furfurylation is known to result in changes in physical properties in comparison with untreated wood (Lande et al 2008) and in the current work results in lower MC compared with untreated wood after a certain time at high RH. Given that water within the cell wall interacts with the carbohydrates through hydrogen bonding and that such interactions will be reflected in the NMR relaxation times, these observations may indicate that the polysaccharides are not modified by furfurylation, but that their hydroxyl groups are not as readily accessible because the furfuryl alcohol polymer to some degree sterically hinders water molecules from approaching hydroxyl groups within wood carbohydrates.

If this interpretation is correct, it implies that the main reason why furfurylation is capable of protecting wood from various types of biological degradation is that it bulks the cell wall so that moisture does not enter as easily as in untreated wood. However, given enough time, RHs close to 100% will permit water to eventually penetrate into the cell walls of furfurylated wood (Venås 2008; Thygesen et al 2009). This is in contrast to acetylation, which is believed to both bulk the cell wall and block wood cell wall hydroxyl groups with covalently bound acetyl groups (Matsuda 1996; Papadopoulos and Hill 2003; Hill et al 2005). The latter implies that water molecules can no longer form hydrogen bonds with the blocked hydroxyl groups regardless of the environment in which the wood is placed.

This explanation notwithstanding, among the difficulties in assigning time domain–NMR peaks for wood is that relaxation times can be affected by more than one parameter. Obviously, the chemical environment in which water is held is of importance, but the physical structure of the wood also plays a role. As pore sizes change, the relaxation time of compartmentalized water changes concomitantly. The bulking of the cell wall attributed to furfurylation or acetylation may, therefore, also influence the relaxation times of the cell wall water through physical interactions. Furthermore, in the present study, in which the weight gain was much higher in the furfurylated than in the acetylated samples, differences in bulking confound chemical differences between the two types of modifications.

CONCLUSIONS

Using LF–TD-NMR, the water in untreated, acetylated, and furfurylated spruce sapwood

was studied below fiber saturation during drying at 40°C.

The study showed that at MC just below fiber saturation, the modified samples held only about one-half the moisture of the untreated samples, but all three sample types had two water populations within the wood cell wall at this point. In an earlier study, in which these sample types were studied above fiber saturation, only one population was found within the fiber wall, most likely because cell lumen water dominated the relaxation curves. The two populations found in the present study had somewhat similar spin–spin relaxation times for the untreated and the furfurylated samples (1 and 0.15 and 0.5 and 0.15 ms, respectively), whereas the relaxation times for the two populations within the acetylated wood both deviated from the other two sample types (1.2 – 3.5 and about 0.1 ms). For the untreated and the furfurylated samples, the two populations merged into one population at 5 – 10% moisture, a population that had the same relaxation time for the two different sample types, and furthermore varied in the same way with MC. For the acetylated wood, the two populations did not merge during drying and had relaxation times that were different from the other two sample types for all MC. These results indicate that while acetylation changed the interaction between water and the wood cell wall, this was only to a limited extent the case for furfurylation. The main effect of furfurylation was a reduction in the amount of water within the wood cell wall at the beginning of the drying experiment.

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