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Janewithayapun, R., Karlsson, H., Hedenqvist, M. et al (2026). Impact of ring-opening chemistry on the local chain mobility of arabinoxylan. Carbohydrate Polymers, 392.  
<http://dx.doi.org/10.1016/j.carbpol.2026.125873>

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# Impact of ring-opening chemistry on the local chain mobility of arabinoxylan<sup>☆</sup>

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## ARTICLE INFO

Dataset link: <https://doi.org/10.5281/zenodo.9210787>

### Keywords:

Wheat bran  
Solid-state NMR  
Hemicellulose  
Chain mobility  
Polymer dynamics

## ABSTRACT

Periodate oxidation and borohydride reduction has been put forward as a modification that increases the flexibility of polysaccharide chains, thereby lowering the glass transition temperature. To investigate whether the reaction is able to increase the chain mobility of a branched polysaccharide such as arabinoxylan (AX), ring-opened dialdehyde AX (DAX), and dialcohol AX (DiolAX) were studied with solid-state NMR techniques. For materials equilibrated at 53% relative humidity, it was found that DiolAX exhibits increased chain mobility, observed as a two- and three-fold decrease in the proton relaxation time in the rotating frame ( $T_{1\rho H}$ ), compared to AX and DAX. From measurements of the proton dipolar linewidth, the narrowest linewidth, thus highest mobility, was observed at the C5/ring-opened C2–C3 region of DiolAX. This is expected largely from an increase in mobility of the ring-opened C2–C3 environments. When the materials were equilibrated at <10% RH, the dynamics became slower and more similar across AX, DAX and DiolAX.

## 1. Introduction

Periodate oxidation to produce dialdehyde groups, allows for cleaving of the specific C–C bonds in polysaccharides (Buist et al., 1971, 1959; Kristiansen et al., 2010). This is typically followed by reduction of the dialdehyde groups to dialcohols for chemical stability. The oxidation–reduction reaction has been performed on several polysaccharides, including: cellulose (Kasai et al., 2014; Larsson et al., 2014; Simon et al., 2024), chitosan (Kristiansen et al., 2010), alginates (Kristiansen et al., 2010; Vold et al., 2006), xylan (Amer et al., 2016; Börjesson et al., 2018; Palasingh et al., 2021), and arabinoxylan (AX) (Börjesson et al., 2018, 2019), leading to increased polysaccharide flexibility (Börjesson et al., 2018; Kristiansen et al., 2010; Simon et al., 2024), and lower glass transition temperature ( $T_g$ ) (Börjesson et al., 2018; Simon et al., 2024).

Through size exclusion chromatography with multi-angle light scattering, the Flory exponent was shown to decrease for dialdehyde cellulose, showing a change in conformation from that of extended chains to partially collapsed chains (Potthast et al., 2007). In the case of alginate, the persistence length, a measure of chain stiffness, was shown to decrease by a factor of 3 after periodate oxidation (Vold et al., 2006). Thermo-mechanically, dialcohol celluloses are more ductile (Larsson et al., 2014; Morooka et al., 1989), and have lower  $T_g$  than their unmodified counterparts (Simon et al., 2024). A lowered  $T_g$  with oxidation has also been observed in dialdehyde xylan by dynamic mechanical analysis (Börjesson et al., 2018).

In branched polysaccharides, such as arabinoxylan (AX), shown in Fig. 1a, ring-opening can occur on both the side groups and the backbone (Fig. 1b–c). For AX, oxidation has been observed to occur more

<sup>☆</sup> This article is part of a Special issue entitled: ‘EPNOE 2025’ published in Carbohydrate Polymers.

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predominantly on the arabinose side groups (Börjesson et al., 2018; Janewithayapun et al., 2024, 2026). Oxidation of AX to dialdehyde AX (DAX) was determined to have no or little effect on the  $T_g$  (Börjesson et al., 2018). Additionally, a study on the chain conformation by solution-state small-angle X-ray scattering (SAXS) (Janewithayapun et al., 2026) showed that oxidation to DAX, and subsequent reduction to dialcohol AX (DiolAX) result in a small decrease in persistence length (by  $\sim 10\%$ ), and does not change the overall chain conformation. Yet, a modification route combining oxidation–reduction (at  $\sim 20\%$  degree of ring-opening) and etherification of AX results in improved material ductility and melt processability, compared to the etherification only (Börjesson et al., 2019).

SAXS and  $T_g$  measurements probe conformation at larger length scales, and slower segmental dynamics, respectively. Both of these are more strongly affected by the AX backbone, rather than the ring-opened side groups. We hypothesize that processes on smaller, more local length scales are responsible for changes in DiolAX mobility. An example could be from increased motions in the ring-opened side groups. Such changes would not significantly affect the chain conformation in solution, and may have been difficult to observe through changes in the  $T_g$ . Solid-state NMR is an excellent tool to investigate local mobility of macromolecules, with the possibility to distinguish the motions of different chemical functional groups and domains (McBrierty & Packer, 1993; Mirau, 2004a; Radloff et al., 1996). In this work, the proton relaxation time in the rotating frame ( $T_{1\rho H}$ ), cross polarization (CP) time constant ( $T_{CH}$ ), and the proton linewidth from a two dimensional wideline separation experiment (WISE) are measured and used to probe the differential dynamics of AX, DAX and DiolAX.

## 2. Experimental

### 2.1. Materials

Sodium metaperiodate ( $\text{NaIO}_4$ ), sodium borohydride ( $\text{NaBH}_4$ ), and sodium phosphate monobasic ( $\text{NaH}_2\text{PO}_4$ ) were purchased from Sigma-Aldrich (Germany). The chemicals were used without further purification. Deionized water was used throughout all experiments. Regenerated cellulose dialysis membrane (Spectra/Por 3) with a molecular weight cutoff of 3.5 kDa was purchased from Spectrum Laboratories (United States).

AX from wheat bran was obtained via alkali extraction and solvent fractionation, and is the same AX0.9 fraction reported in Janewithayapun et al. (2024). This fraction of AX has an arabinose:xylose ratio of 0.9, and a weight-averaged molar mass  $M_w$  of  $330 \text{ kg mol}^{-1}$ . The detailed monosaccharide composition and glycosidic linkage analysis results were measured based on methods developed by Pettolino et al. (2012) with modifications as reported in Janewithayapun et al. (2025), and are shown in Table S1 of the supplementary information.

### 2.2. Preparation of dialdehyde AX

For periodate oxidation, 25 mL of an aqueous solution of AX at a concentration of  $20 \text{ mg mL}^{-1}$  (containing  $3.785 \text{ mmol}$  anhydroxylose unit (AXU) of AX, with molecular weight of  $132.1 \text{ g mol}^{-1}$ ) was heated at  $70^\circ\text{C}$  for 3 h, followed by heating at  $90^\circ\text{C}$  for 10 min to achieve dissolution of AX. After allowing the solution to cool, isopropanol ( $1.25 \text{ mL}$ ) was added to act as a radical scavenger (Painter, 1988) and water was added to reach a final volume of  $25 \text{ mL}$ . Then,  $\text{NaIO}_4$  ( $0.2 \text{ g}$ ,  $0.946 \text{ mmol}$ ,  $0.25 \text{ equiv.}$ ) was added to initiate the oxidation reaction. The reaction flask was covered with aluminium foil to protect from light and stirred at room temperature for 20 h, when no further changes were observed in the  $\text{NaIO}_4$  concentration measured using the UV–Vis method described below. The reaction mixture was then transferred to a dialysis membrane and dialyzed with repeated changes of water for 48 h, then freeze-dried to obtain DAX.

### 2.3. Preparation of dialcohol AX

The oxidation procedure above was repeated for  $100 \text{ mL}$  of AX solution ( $15.14 \text{ mmol}$  AXU) with the same equivalents of reagents but without isolation of the material. After completion of the oxidation reaction,  $\text{NaH}_2\text{PO}_4$  ( $0.15 \text{ g}$ ,  $1.25 \text{ mmol}$ ,  $0.08 \text{ equiv.}$ ) and  $\text{NaBH}_4$  ( $1 \text{ g}$ ,  $26.43 \text{ mmol}$ ,  $1.75 \text{ equiv.}$ ) were dispersed in water ( $25 \text{ mL}$ ), then added to the AX reaction mixture. The reaction mixture was stirred for 4 h at room temperature, after which the mixture was transferred to dialysis membranes and dialyzed with repeated changes of water for 48 h. The mixture was then freeze-dried to obtain DiolAX.

### 2.4. Degree of oxidation (DO) from UV–Vis spectroscopy

The progress of the oxidation reaction was followed with ultraviolet spectroscopy (UV–Vis) (Cary 60 UV–Vis, Agilent Technologies, United States) using the absorption band at  $\lambda = 290 \text{ nm}$ , corresponding to the concentration of  $\text{NaIO}_4$  (Maekawa et al., 1986). A linear standard curve for the periodate solution was obtained using concentrations of  $\text{NaIO}_4$  between  $0.1 \text{ mM}$  to  $5 \text{ mM}$ . The DO from UV–Vis was calculated from the consumption of  $\text{NaIO}_4$  by making the assumption that the consumption of  $1 \text{ mol}$   $\text{NaIO}_4$  results in the oxidation of  $1 \text{ mol}$  of arabinose or xylose. In previous work, it was shown that UV–Vis values of the DO are in agreement with those measured by solution state  $^{13}\text{C}$  NMR (Janewithayapun et al., 2026), differing by 3%–4% values of DO at this  $\text{NaIO}_4$  equivalent.

### 2.5. Small-angle X-ray scattering

SAXS experiments were performed at the CoSAXS beamline at MAX IV laboratory, Lund, Sweden. An X-ray wavelength ( $\lambda$ ) of  $1.0 \text{ \AA}$  was used, with detection on a SAXS detector; Eiger2 4M (Dectris AG, Switzerland), and a wide-angle X-ray scattering (WAXS) detector; Pilatus3 2M (Dectris AG, Switzerland). The sample to detector distance was  $10.12 \text{ m}$  for the SAXS detector and  $0.57 \text{ m}$  for the WAXS detector, giving a  $q$  range of  $0.0013 \text{ \AA}^{-1}$  to  $0.94 \text{ \AA}^{-1}$ . Data reduction was carried out using the Python implementation of MatFRAIA (Jensen et al., 2022) for radial integration, followed by correction for dark contribution, X-ray beam transmittance and scaled to water absolute intensity.

### 2.6. Humidity conditioning and determination of moisture content

Freeze-dried AX, DAX and DiolAX materials were stored for over 48 hours, in sealed jars with a low or high humidity environment, corresponding to  $< 10\%$  and  $53\% \text{ RH}$ , respectively. The RH was controlled using silica gel for the  $< 10\% \text{ RH}$  jar, which reliably kept humidity at  $7\%$ – $8\% \text{ RH}$  for over one week, tested using a Sensirion SHT31 sensor. For the  $53\% \text{ RH}$ , a saturated  $\text{Mg}(\text{NO}_3)_2$  solution was added to a sealed jar.

The moisture content in the materials was determined with dynamic vapor sorption (DVS), using the DVS Advantage 1 (Surface Measurement Systems, United Kingdom). Measurements were done with a sorption process followed by a desorption process. The humidity inside the measurement chamber was stepped from  $0\%$  partial pressure ( $P/P_0$ ) to  $90\% P/P_0$ , and back to  $0\% P/P_0$  in steps of  $10\%$ , with exception of  $50\%$  being replaced with  $53\%$  to match the RH of the saturated  $\text{Mg}(\text{NO}_3)_2$  solution. At each step, the humidity was held constant until the rate of change in mass ( $dm/dt$ ) was below  $0.002\%$  per min over an evaluation window of 5 min. The reference mass for calculating the moisture content was taken as the mass at the end of the first  $0\% P/P_0$  step.

### 2.7. Solid-state NMR

Solid-state MAS experiments were performed in a  $16.4 \text{ T}$  magnetic field on the Bruker Avance III HD spectrometer equipped with a  $4 \text{ mm}$

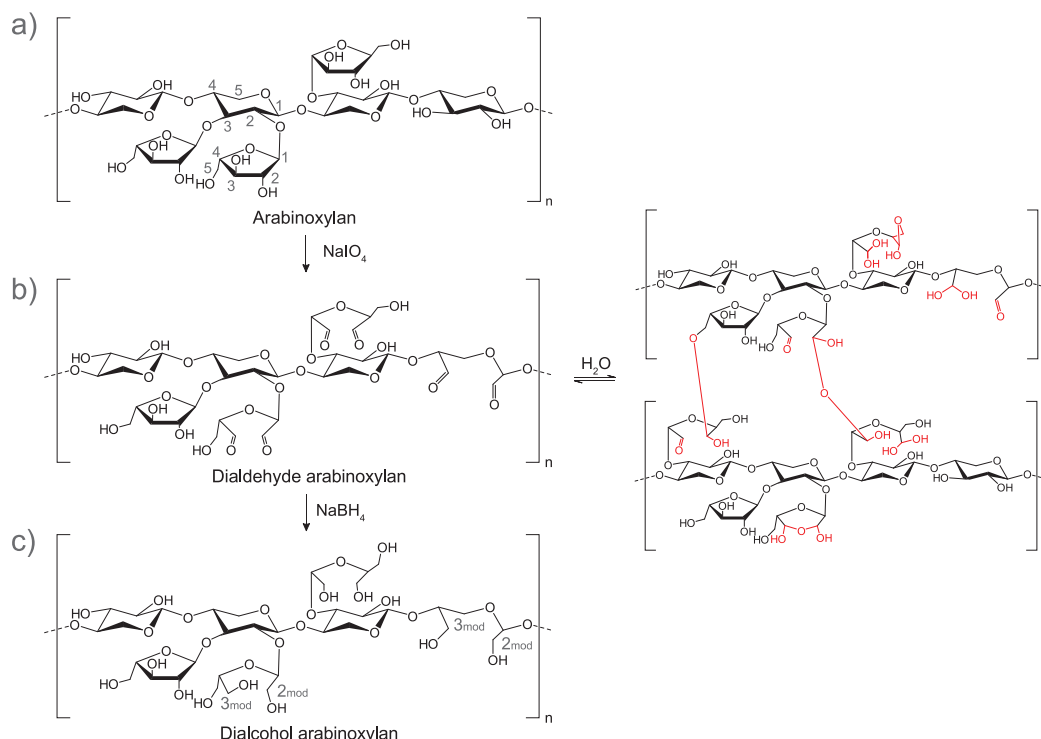


**Fig. 1.** Schematic representation of the chemical structure of a) arabinoxylan, b) dialdehyde arabinoxylan and c) dialcohol arabinoxylan with labeling of the carbon nuclei number.  $2_{\text{mod}}$  and  $3_{\text{mod}}$  indicate the ring-opened carbon nuclei. The red colored sections show possible side reactions in oxidized DAX.

HXY MAS probe operating in  $^1\text{H}/^{13}\text{C}$  double-resonance mode at a MAS rate of 4 kHz. Carbon spectra ( $^1\text{H}$ - $^{13}\text{C}$  CP) were acquired with 512 scans, a relaxation delay of 3 s and an acquisition time of 6 ms. The  $^1\text{H}$  90° pulse was 3.03  $\mu\text{s}$ . The CP mixing time was between 25  $\mu\text{s}$  and 10 ms and employed 80%–100% ramp on the  $^1\text{H}$  channel at 42 kHz rf field strength, and with rf field strength of 38 kHz on the  $^{13}\text{C}$  channel. The SPINAL-64 program was used for  $^1\text{H}$  decoupling during acquisition with a field strength of 100 kHz.

Phasing and baseline correction was performed in TopSpin 4.3.0. Integration and fitting of data to obtain  $T_{1\rho\text{H}}$  and  $T_{\text{CH}}$  was done with a custom Python script. Integration regions were, for AX and for modified DAX/DiolAX: C1 (114.8–98.8 ppm), C2/C3/C4 (92.8–66.5 ppm), C5 or C5/C2<sub>mod</sub>/C3<sub>mod</sub> (66.5–56 ppm). Fitting of the integrated intensities were performed using the Levenberg–Marquardt algorithm implemented in SciPy (Virtanen et al., 2020), without weights. The buildup and decay of the  $^{13}\text{C}$  signals was described by Eq. (1) (Bardet et al., 2007; Mirau, 2004b).

$$M(t_{\text{cp}}) = M_{\text{eq}}(1 - e^{-t_{\text{cp}}/T_{\text{CH}}})e^{-t_{\text{cp}}/T_{1\rho\text{H}}} \quad (1)$$

where  $M(t_{\text{cp}})$  is the measured intensity at CP contact time  $t_{\text{cp}}$  and the equilibrium magnetization intensity ( $M_{\text{eq}}$ ),  $T_{1\rho\text{H}}$ , and  $T_{\text{CH}}$  are fitted parameters.

2D  $^1\text{H}$ - $^{13}\text{C}$  HETCOR experiments were recorded with 64 scans, 32 points with an increment of 7.15  $\mu\text{s}$  in the indirect  $^1\text{H}$  dimension and 300  $\mu\text{s}$  CP contact time with the same CP conditions as mentioned above. 2D  $^1\text{H}$ - $^{13}\text{C}$  WISE experiments were conducted with the same settings as the HETCOR experiment, adding a  $^1\text{H}$  spin diffusion period varying from 10  $\mu\text{s}$  to 10 ms. The projection of the  $^1\text{H}$  dimension was taken from the 2D data, and the narrow component intensity was obtained by integrating from –2 ppm to 12 ppm along the  $^1\text{H}$  dimension. The narrow component intensity buildup as a function of mixing time was fitted to Eq. (2), similar to the approach used by Holland et al. (2004) but modified to take into account the broad intensity component which does not change with mixing time.

$$I(t_m) = A \times \begin{cases} a\sqrt{t_m} + (1 - a\sqrt{t_m^*}) & t_m \leq t_m^* \\ 1 & t_m > t_m^* \end{cases} \quad (2)$$

where  $t_m$  is the mixing time, and  $t_m^*$  is the cross-over point between the buildup and the plateau-like region at longer mixing times.  $A$  and  $a$  are fitting constants accounting for intensity scaling factor and offset. Integration and fitting of the intensity buildup was done in EasyNMR (<https://easynmr.csdm.dk/>) (Juhl et al., 2020; Koppe et al., 2025).

## 2.8. Fourier transform infrared spectroscopy

Samples after the NMR experiment were dried in a vacuum oven overnight at 50 °C. They were then characterized by Fourier transform infrared spectroscopy (FTIR) using a Nicolet iS50 spectrometer in attenuated total reflection (ATR) mode. Spectra were obtained between 4000–400  $\text{cm}^{-1}$  with 4  $\text{cm}^{-1}$  resolution, 32 scans, and measured in duplicate. Background was taken after every spectrum and subtraction performed using the OMNIC 9.9.535 software.

## 3. Results and discussion

### 3.1. Results of the oxidation and reduction reactions

The oxidation reaction for DAX indicated a  $\text{NaIO}_4$  consumption of 92%, and for DiolAX, measured prior to reduction, of 99%. These consumption values give estimated values (within 3–4 absolute % values (Janewithayapun et al., 2026)) for the DO as 23% and 25% in DAX and DiolAX, respectively. The success of oxidation and reduction steps were further confirmed by solid-state  $^{13}\text{C}$  NMR spectra of AX, DAX and DiolAX (Fig. 2), and by ATR-FTIR (Fig. 3). In Fig. 2a, the spectra of samples equilibrated at 53% RH, and at the CP mixing time which gave the highest C1 intensity are shown: 0.3 ms, 0.5 ms, and 0.15 ms for AX, DAX and DiolAX, respectively. Fig. 2b shows the NMR spectra for materials equilibrated at ~10% RH at CP mixing times of 0.5 ms, 0.3 ms, and 0.4 ms for AX, DAX, and DiolAX. Each spectrum was subsequently normalized so that the integral of all signals between 50–140 ppm equaled 1.

No aldehyde signals were present in the  $^{13}\text{C}$  NMR spectra of DAX, expected in the 170–200 ppm region (insets of Fig. 2). This was

true for data at all CP mixing times (data not shown). However, the CP efficiency of carbonyl groups are low (Jacob & Falourd, 2025), and so, small populations of carbonyl groups may not be detected by this method. Instead, we observed an increase in intensity around the 90 ppm region, which is associated to hemialdal and hemiacetal functionalities, occurring from reactions between free aldehyde groups and water (Amer et al., 2016; Leguy et al., 2018; Münster et al., 2017). In the FTIR spectra of DAX (Fig. 3), weak carbonyl stretching signals were visible at  $1730\text{ cm}^{-1}$ . A change in shape of the strong absorption region between  $1000\text{--}1100\text{ cm}^{-1}$  was also observed, accompanied by a weak signal at  $870\text{ cm}^{-1}$ . Signals in these regions are assigned to C–O stretching vibrations in different functional groups, and their increase have been reported to be associated with the formation of hemiacetal (López Durán et al., 2016; Lucia et al., 2020; Plappert et al., 2018) and hemialdal groups (Amer et al., 2016; Plappert et al., 2018) in dialdehyde polysaccharides.

Based on the presented data and previous studies of similar dialdehyde derivatives (Amer et al., 2016; Guigo et al., 2014; Kim et al., 2000; Leguy et al., 2018; Münster et al., 2017; Palasingh et al., 2021), the DAX spectra are consistent with the presence of aldehyde-derived functionalities. Possible structures include hydrated aldehydes, and intra- or inter-chain hemialdal and hemiacetal functionalities, highlighted in red in Fig. 1b, adapted from those presented for xylan and cellulose (Amer et al., 2016; Münster et al., 2017; Palasingh et al., 2021; Plappert et al., 2018).

After reduction of DAX to DiolAX, the  $^{13}\text{C}$  NMR spectra showed a strong increase in the intensity of signals in the C5 region of DiolAX. This is an indication that the AX rings have been opened, resulting in an upfield shift of the C2 and C3 carbons to around 63 ppm, where they overlap with the C5 signal (Janewithayapun et al., 2026; Karlsson et al., 2024; Leguy et al., 2018; Palasingh et al., 2021). The intensity in the 90 ppm region of DiolAX has also been lowered to a comparable intensity with AX, indicating the successful reduction of the hemiacetal and hemialdal structures (Leguy et al., 2018). As our CP/MAS sequence did not include multiple CP steps, and therefore, was not quantitative, we only perform a qualitative assessment of the chemical structure changes. In the FTIR spectra of DiolAX, the disappearance of the carbonyl signal at  $1730\text{ cm}^{-1}$ , and further changes in the C–O stretching region also indicate the success of the reduction reaction.

### 3.2. Chain conformation by SAXS

Solution-state SAXS was performed using the analytical approach presented in Janewithayapun et al. (2026). Measurements of a separate set of DAX has shown that aggregation prevents a full analysis of the chain conformation (Janewithayapun et al., 2026), hence only AX and DiolAX were analyzed. The form factor of AX and DiolAX was fitted with a flexible cylinder model (Janewithayapun et al., 2025; Pedersen & Schurtenberger, 1996, 2004), with results shown in Figure S1 of the supplementary information. The obtained chain persistence lengths were  $4.36 \pm 0.1\text{ nm}$  and  $4.0 \pm 0.1\text{ nm}$  for AX and DiolAX, respectively, and the general scattering features appeared similar between the two. The extent of persistence length reduction of around 10%, and the unchanging scattering features from AX to DiolAX are consistent with previous experiments on a different batch of AX materials (Janewithayapun et al., 2026). In contrast to, for example, a decrease in persistence length by a factor of 3, for oxidized alginate (Vold et al., 2006). The further absence of change in the intermediate  $q$  slope, representing the Flory exponent of the chain, indicate no folding or collapsing of the DiolAX chains as a result of increased flexibility. Therefore, the SAXS results show that mobility changes observed by NMR would not be primarily due to a large change in the AX backbone's chain conformation.

### 3.3. Moisture content of materials

The sorption and desorption isotherms of the freeze dried materials are shown in Figure S2 of the supplementary information. The shape

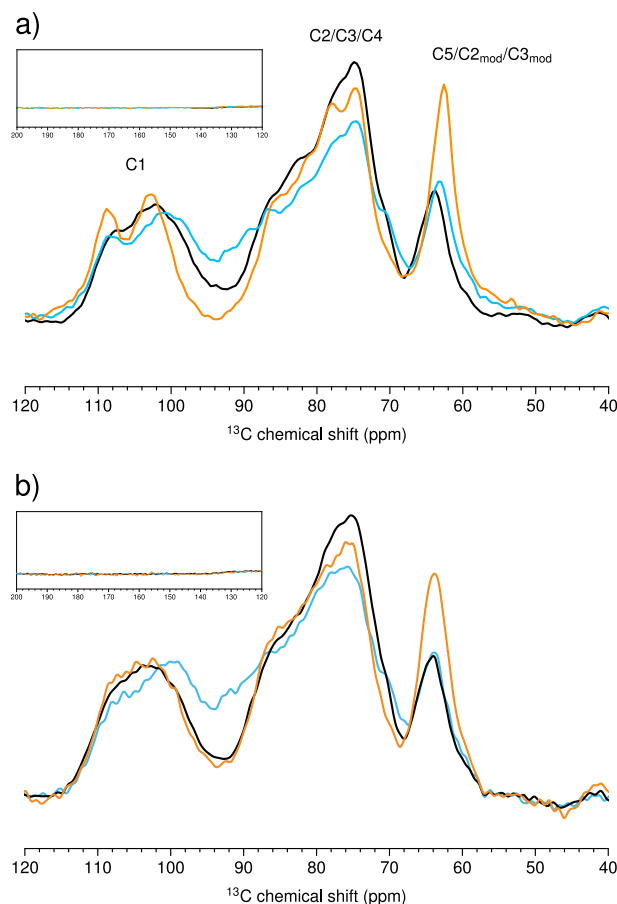


Fig. 2. Comparison of the  $^{13}\text{C}$  CP/MAS NMR spectra of arabinoxylan (black), dialdehyde arabinoxylan (blue) and dialcohol arabinoxylan (orange), with total integral normalized to 1. The inset shows the  $^{13}\text{C}$  intensities at higher ppm, where carbonyl signals would be expected to appear. a) shows spectra of samples equilibrated at 53% RH, and b) shows spectra of samples equilibrated at 10% RH.

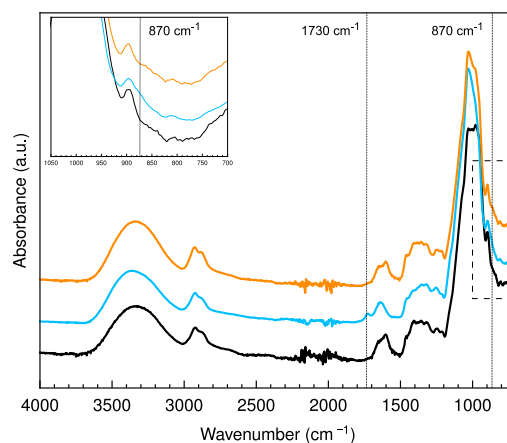


Fig. 3. ATR-FTIR spectra of dry arabinoxylan (black), dialdehyde arabinoxylan (blue) and dialcohol arabinoxylan (orange). Dotted lines indicate carbonyl signals at  $1730\text{ cm}^{-1}$ , and of hemialdal, -acetal signals at  $870\text{ cm}^{-1}$ . Dashed box indicates the region magnified in the inset.

**Table 1**

Moisture content of arabinoxylan (AX), dialdehyde arabinoxylan (DAX) and dialcohol arabinoxylan (DiolAX), and values of  $T_{CH}$  and  $T_{1\rho H}$  obtained from fitting the development of the  $^{13}C$  integral intensity to Eq. (1).

| 53% RH | Moisture content<br>(% wt.) | $T_{CH}$ ( $\mu s$ ) | C1<br>$T_{1\rho H}$ (ms) | C2/C3/C4<br>$T_{CH}$ ( $\mu s$ ) | $T_{1\rho H}$ (ms) | C5/C2 <sub>mod</sub> /C3 <sub>mod</sub><br>$T_{CH}$ ( $\mu s$ ) | $T_{1\rho H}$ (ms) |
|--------|-----------------------------|----------------------|--------------------------|----------------------------------|--------------------|-----------------------------------------------------------------|--------------------|
| AX     | 9                           | 46 ( $\pm 6$ )       | 3.0 ( $\pm 0.3$ )        | 43 ( $\pm 5$ )                   | 3.0 ( $\pm 0.3$ )  | 33 ( $\pm 3$ )                                                  | 2.7 ( $\pm 0.2$ )  |
| DAX    | 10                          | 59 ( $\pm 7$ )       | 3.8 ( $\pm 0.4$ )        | 47 ( $\pm 7$ )                   | 3.9 ( $\pm 0.3$ )  | 30 ( $\pm 4$ )                                                  | 4.1 ( $\pm 0.4$ )  |
| DiolAX | 10                          | 39 ( $\pm 3$ )       | 1.3 ( $\pm 0.1$ )        | 40 ( $\pm 3$ )                   | 1.3 ( $\pm 0.1$ )  | 47 ( $\pm 4$ )                                                  | 1.4 ( $\pm 0.1$ )  |
| 10% RH | Moisture content<br>(% wt.) | $T_{CH}$ ( $\mu s$ ) | C1<br>$T_{1\rho H}$ (ms) | C2/C3/C4<br>$T_{CH}$ ( $\mu s$ ) | $T_{1\rho H}$ (ms) | C5/C2 <sub>mod</sub> /C3 <sub>mod</sub><br>$T_{CH}$ ( $\mu s$ ) | $T_{1\rho H}$ (ms) |
| AX     | 2                           | 57 ( $\pm 8$ )       | 4.2 ( $\pm 0.4$ )        | 53 ( $\pm 6$ )                   | 4.3 ( $\pm 0.4$ )  | 40 ( $\pm 5$ )                                                  | 4.2 ( $\pm 0.4$ )  |
| DAX    | 4                           | 51 ( $\pm 7$ )       | 3.6 ( $\pm 0.4$ )        | 42 ( $\pm 6$ )                   | 3.8 ( $\pm 0.4$ )  | 38 ( $\pm 5$ )                                                  | 3.8 ( $\pm 0.4$ )  |
| DiolAX | 3                           | 60 ( $\pm 9$ )       | 3.1 ( $\pm 0.4$ )        | 51 ( $\pm 6$ )                   | 3.1 ( $\pm 0.3$ )  | 35 ( $\pm 3$ )                                                  | 2.9 ( $\pm 0.2$ )  |

of the sorption and desorption isotherms for the AX and the DiolAX materials were similar for the full range of P/P<sub>0</sub> (or % RH) tested. The isotherms of the DAX differed from those of AX and DiolAX at P/P<sub>0</sub> above 80% (or 80% RH), above which the DAX had lower moisture content. In the desorption isotherm, DAX exhibited larger hysteresis compared to the other two materials. The larger hysteresis for DAX appears similar to those of dialdehyde cellulose (Larsson et al., 2008), although a lower maximum moisture absorption was observed in our DAX. As moisture uptake in dialdehyde cellulose is dependent on the breaking of the hemiacetal and hemialdal functionalities (Larsson et al., 2008), it is possible that similar functionalities in DAX were not converted to aldehydes under our measurement conditions. The lower hysteresis in AX and DiolAX agree with measurements on dialcohol cellulose, where Salmén and Larsson (2018) proposed that moisture hysteresis is inversely proportional to material stiffness. That is, materials near their softening temperatures have lower moisture hysteresis (Salmén & Larsson, 2018). Hence, our DVS measurements suggest a higher degree of rigidity in DAX chains, compared to AX and DiolAX.

With regards to the moisture content of the materials measured in the solid-state NMR experiments, samples in this work were equilibrated between 0% RH and 53% RH, without prior exposure to high humidity i.e., similar to the sorption isotherm, where AX, DAX and DiolAX can be considered to behave similarly with increasing RH. The moisture content of the packed NMR samples were estimated from DVS equilibrium data, shown in Table 1, referenced against the equilibrium mass at 0% RH for each material. The RH inside the silica gel jar was around 7%–8% RH, therefore, the moisture content of these samples were taken from the nearest DVS data point at 10% RH. Each sample's conditioning environment will subsequently be denoted as 10% RH for samples stored in the silica jar, and 53% RH for samples stored in the Mg(NO<sub>3</sub>)<sub>2</sub> jar.

### 3.4. Dynamics from CP/MAS with variable contact time

With the general assumptions  $T_{1\rho H} \gg T_{CH}$  and the carbon relaxation time  $T_{1\rho C} \gg T_{CH}$ , the intensity at contact time  $t$  is described according to Eq. (1) (Mirau, 2004b). The intensity increases as a result of polarization transfer from the protons to the carbons, with the transfer efficiency represented by the CP time constant  $T_{CH}$ . The decay in intensity occurs as a result of  $T_{1\rho H}$  relaxation, which is sensitive to motions on the kHz timescale (Mirau, 2004b). The development of the carbon signal intensity at the C1 position is shown in Fig. 4. Due to spin diffusion, all the carbon nuclei in the same sample share similar  $T_{1\rho H}$ , and decay similarly, here only the C1 is shown for visual clarity. Data and fits for all nuclei are presented in Figure S3 of the supplementary information.

For the materials stored at 53% RH, the integral of C1 in DiolAX showed a faster decay in intensity compared to AX (Fig. 4a). The  $T_{1\rho H}$  obtained after fitting of the decay with Eq. (1) is lower by a factor of 2–2.3 for DiolAX compared to those obtained for AX, independent of the  $^{13}C$  chemical shift (Table 1). The  $T_{1\rho H}$  of DAX was 1.3–1.5 times larger than that of AX, which may be related to restricted mobility from

intra- or inter-chain associations caused by transient aldehyde groups. From the fitted values for  $T_{CH}$ , we also observed a change in trend in the DiolAX. In the other samples, between all three regions,  $T_{CH}$  were larger for C1 and C2/C3/C4, whereas in DiolAX,  $T_{CH}$  is largest for C5/C2<sub>mod</sub>/C3<sub>mod</sub>.

For AX, DAX and DiolAX materials stored at 10% RH (Fig. 4b), the decay in intensity of the signals are slower, and more similar between the samples. Compared to respective counterpart stored at 53% RH, the fitted  $T_{1\rho H}$  for AX was larger by a factor of  $\sim 1.5$  at 10% RH, and for DiolAX, by a factor of  $\sim 2$ . Interestingly, the  $T_{1\rho H}$  of DAX showed little moisture sensitivity, in fact, the fitted  $T_{1\rho H}$  were slightly lower for the sample stored at 10% RH. The trends for  $T_{CH}$  for DiolAX also become similar to the other two samples;  $T_{CH}$  being highest for C1 and lowest for C5/C2<sub>mod</sub>/C3<sub>mod</sub>.

The lower  $T_{1\rho H}$  of DiolAX indicates that there is an increase in motions of the chains compared to AX and DAX, with correlation time in the 10  $\mu s$  to 100  $\mu s$  range (frequencies of 100 kHz to 10 kHz) (McBrierty & Packer, 1993; Mirau, 2004a). Furthermore, as seen from the larger  $T_{1\rho H}$  for DiolAX 10% RH, these motions are reduced at lower moisture contents. The unmodified AX also showed lower  $T_{1\rho H}$  at 53% RH, demonstrating the plasticization effect of water on these two materials, whereas the DAX was less affected, which may again be related to the restrictions caused by the transient aldehyde groups. Plasticization increases free volume in polymer chain systems, and disrupts intermolecular bonds, both of which facilitate bond rotation and chain mobility (Hodge et al., 1996). These results are consistent with increased mobility in the ring-opened DiolAX structure, occurring under hydrated conditions. Similar observations were made of the mechanical properties of cellulose and dialcohol cellulose materials, where the ring-opened dialcohol cellulose were more strongly plasticized by moisture compared to the starting cellulose material (Larsson et al., 2014).

As mentioned above,  $T_{1\rho H}$  is affected by spin diffusion (Mirau, 2004a), hence all carbon signals in DiolAX share similar  $T_{1\rho H}$ , and their individual dynamics cannot be distinguished by  $T_{1\rho H}$ . However, we had observed that the fitted  $T_{CH}$  was larger for C5/C2<sub>mod</sub>/C3<sub>mod</sub>, relative to the other signals, only in DiolAX at 53% RH. Since molecular motions that average out the dipole–dipole interactions lead to lower CP buildup efficiency (Voelkel, 1988), we interpret the larger  $T_{CH}$  for the C5/C2<sub>mod</sub>/C3<sub>mod</sub> region as an indication that this region contains environments with higher mobility. Although, because of the chemical shift overlap, individual contributions from C5, C2<sub>mod</sub>, C3<sub>mod</sub> cannot be distinguished.

### 3.5. 2D $^1H$ - $^{13}C$ wideline-separation NMR experiments

The mobility of the carbon environments of the AX derivatives was further studied with the 2D WISE experiment. Large-amplitude motions faster than dipolar coupling (50 kHz) lead to a reduction of the proton dipolar line width (Schmidt-Rohr et al., 1992), as such, a qualitative comparison of mobile and rigid segments of the chain can be made. Radloff et al. (1996) showed that sharp water signals were not detected

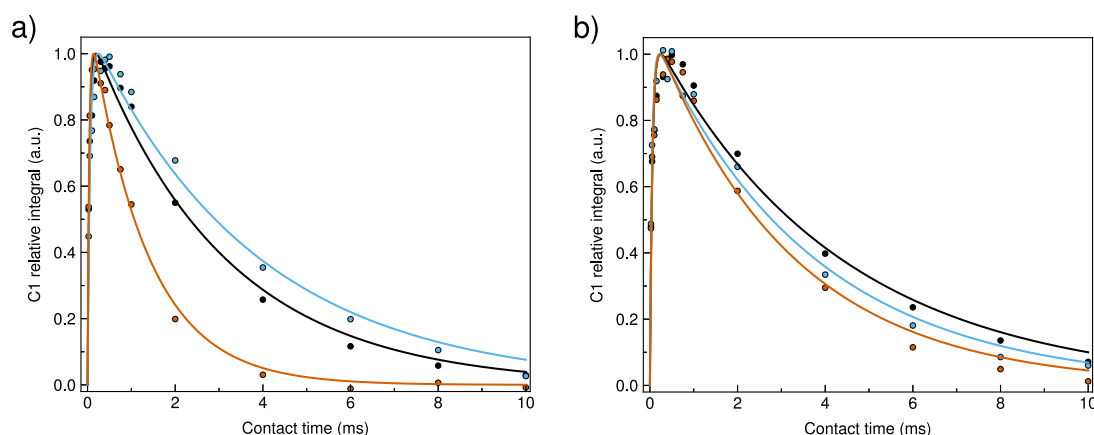


**Fig. 4.** C1 integrals relative to their maximum values as a function of cross-polarization contact time for arabinoxylan (black), dialdehyde arabinoxylan (blue) and dialcohol arabinoxylan (orange) stored at a) 53% RH and b) 10% RH. Lines show fits to Eq. (1).

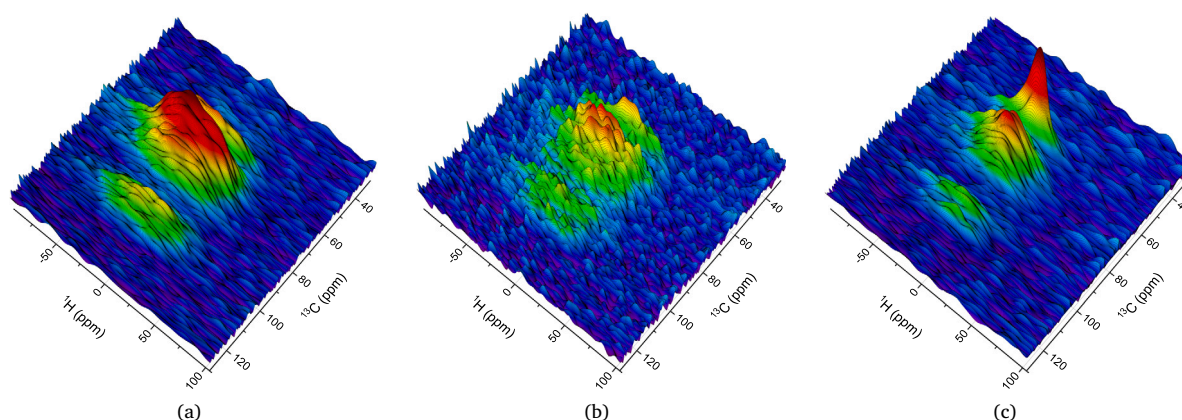


**Fig. 5.** 2D wideline-separation NMR spectra with CP time = 0.3 ms, mixing time = 0.01 ms, for samples equilibrated at 53% RH, a) arabinoxylan, b) dialdehyde arabinoxylan and c) dialcohol arabinoxylan.

for cellulose at short mixing times (mixing time of 0 ms and CP time of 2 ms), as there was insufficient time for spin diffusion between water protons and cellulose aliphatic protons. Only at a mixing time of 5 ms were water signals observed. Therefore, in our WISE experiment with a CP time of 0.3 ms, and a mixing time of 0.01 ms, the spectra should be dominated by signals from the CH and CH<sub>2</sub> groups of AX polymers (Radloff et al., 1996).

The WISE 2D plots for the 0.01 ms mixing time experiments for the three materials stored at 53% RH are shown in Fig. 5a-c. The linewidths of AX and DAX are broader than DiolAX. An estimation of the full width at half maximum (FWHM) by a Lorentzian function, using SciPy, gives FWHM of 43–55 kHz, and 28–45 kHz for AX and DAX respectively. Note that the lower intensity of the broader signals affected the fitting process. The broader signals agree with measurements on cellulose (Radloff et al., 1996) and show that the polymer backbone of AX and DAX are immobile. On the other hand, the spectra of DiolAX show a clear sharp peak (Fig. 5c) in the C5/C2<sub>mod</sub>/C3<sub>mod</sub> region (56–66.5  $^{13}\text{C}$  ppm) with a FWHM of 18 kHz. The other peaks in DiolAX are broader, with FWHM of around 24–30 kHz (Table 2). The narrower linewidth of C5/C2<sub>mod</sub>/C3<sub>mod</sub> point toward a higher prevalence of motions associated with these carbon environments in DiolAX, in agreement with the larger value of  $T_{\text{CH}}$  obtained from the CP/MAS experiments. We would also reason that the motions are more likely associated to the ring-opened C2<sub>mod</sub> and C3<sub>mod</sub>, rather than the unmodified C5. With increasing mixing time to 1 ms and 2.5 ms, AX and DAX exhibited a narrowing of the linewidth as a result of spin diffusion from mobile

water protons, shown in Fig. 6, similar to that observed in cellulose (Radloff et al., 1996). The linewidth of DiolAX showed some narrowing, but to a much smaller extent, as the linewidths were narrow from the start. The narrower linewidth observed in DiolAX at the mixing time of 0.01 ms therefore, supports an increased mobility coming from the DiolAX polymer itself.

The buildup of the narrow component intensity with mixing time is shown in Figure S5 of the supplementary information. The cross-over mixing time ( $\tau_m^*$ ) between the buildup and the plateau-like region at longer mixing times is related to the domain distance (Holland et al., 2004), here between water and AX. All three materials have  $\tau_m^*$  of less than 5 ms (Table 2), indicating distances of less than 1 nm, which could be attributed to water bound to AX chains at the molecular level. This is in comparison to  $\tau_m^*$  of the order of 50 ms which indicate inhomogeneity length scale of around ~3 nm (Radloff et al., 1996).

For the samples stored at 10% RH, the linewidth of DiolAX in the C5/C2<sub>mod</sub>/C3<sub>mod</sub> region broadens (Figure S4, supplementary information), with similar linewidths to AX or DAX at 53% RH in Fig. 5a-b. These results are in agreement with the larger  $T_{1\rho\text{H}}$  and  $T_{\text{CH}}$  from CP/MAS, and show that the increased mobility in DiolAX is not observed at low moisture contents. Furthermore, at longer mixing times, the linewidths of the three 10% RH materials display negligible line narrowing compared to the samples kept at 53% RH (Fig. 6). Similar plots of the narrow component intensity for the 10% RH materials are shown in Figure S5 (supplementary information). A lower intensity was observed overall, correlating well with the lower moisture content.

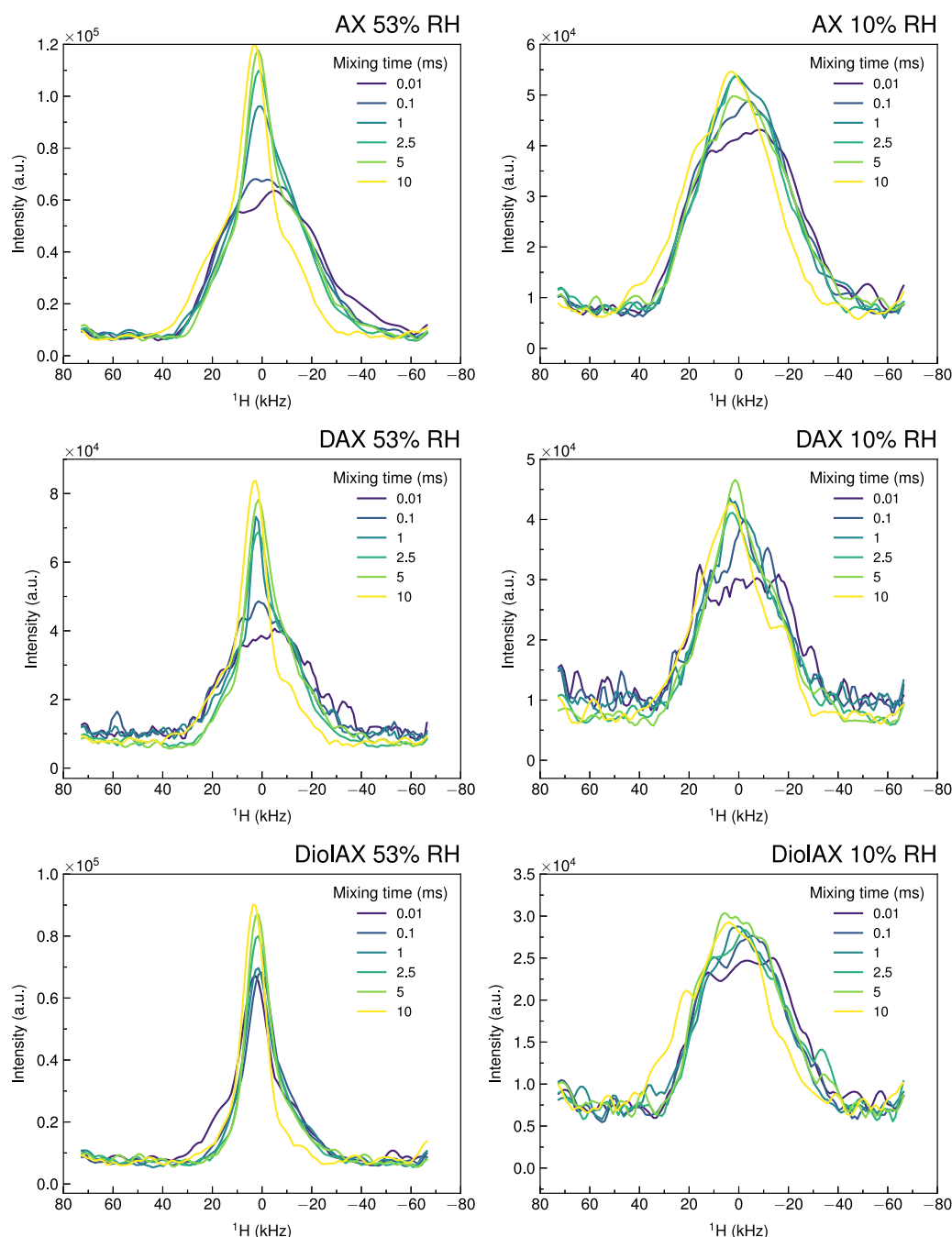


**Fig. 6.**  $^1\text{H}$  1D projection of the sum over the  $^{13}\text{C}$  dimension from wideline-separation experiments, with colors indicating the different mixing times. From top to bottom: arabinoxylan (AX), dialdehyde arabinoxylan (DAX) and dialcohol arabinoxylan (DiolAX). Samples equilibrated at 53% RH are shown in the left column, and those equilibrated at 10% RH in the right column.

Obtained values of  $\tau_m^*$  were lower, which suggests that remaining moisture in the samples are bound closer to the AX chains, but it should be noted that the fitting are also affected by the lower intensity, which gives lower signal to noise ratios.

#### 4. Conclusions

Increased motions of the polysaccharide chain were observed when AX was oxidized and reduced to the ring-opened DiolAX with a DO of 25%. This was seen through a two- to three-fold decrease in  $T_{1\rho\text{H}}$  for DiolAX compared to AX and DAX, obtained from a CP/MAS experiment with variable contact time. The mobility was observed only in the DiolAX stored at 53% RH (moisture content of 10 wt%), also

showing the significant role of water as a plasticizer. Through 2D wideline separation experiments, narrow proton linewidths were observed for DiolAX at 53% RH in the  $\text{C5/C2}_{\text{mod}}/\text{C3}_{\text{mod}}$  region, whereas broader peaks were observed for all other carbon signals and samples. As narrowing of the proton linewidth can be linked to increased molecular motion, the observed narrow linewidths point toward the higher mobility of this region, which is expected to be predominantly from changes in the ring-opened  $\text{C2}_{\text{mod}}/\text{C3}_{\text{mod}}$  environments of DiolAX. This fundamental understanding helps explain how ring-opening can improve modified AX materials' properties when included as part of a modification sequence, despite ring-opening not affecting the AX backbone the same way it does for linear polysaccharides at this DO

**Table 2**

Full width at half maximum (FWHM) of the carbon signals in the  $^1\text{H}$  dimension estimated by a fit to a Lorentzian function, and the cross-over mixing time  $\tau_m^*$  between the buildup and the plateau-like region at longer mixing times. *Arabinoxylan* (AX), *dialdehyde arabinoxylan* (DAX), and *dialcohol arabinoxylan* (DiolAX).

|        | 53% RH | C1/(C1 <sub>mod</sub> )<br>FWHM (kHz) | C2/C3/C4<br>FWHM (kHz) | C5/(C2 <sub>mod</sub> /C3 <sub>mod</sub> )<br>FWHM (kHz) | $\tau_m^*$<br>(ms)  |
|--------|--------|---------------------------------------|------------------------|----------------------------------------------------------|---------------------|
| AX     |        | 43 ( $\pm 2$ )                        | 55 ( $\pm 2$ )         | 51 ( $\pm 2$ )                                           | 2.0 ( $\pm 0.5$ )   |
| DAX    |        | 31 ( $\pm 3$ )                        | 45 ( $\pm 2$ )         | 28 ( $\pm 2$ )                                           | 3.5 ( $\pm 0.6$ )   |
| DiolAX |        | 30 ( $\pm 2$ )                        | 24 ( $\pm 4$ )         | 18 ( $\pm 1$ )                                           | 1.3 ( $\pm 0.2$ )   |
| 10% RH |        |                                       |                        |                                                          |                     |
| AX     |        | 56 ( $\pm 4$ )                        | 61 ( $\pm 3$ )         | 61 ( $\pm 5$ )                                           | 0.16 ( $\pm 0.06$ ) |
| DAX    |        | 61 ( $\pm 11$ )                       | 68 ( $\pm 5$ )         | 52 ( $\pm 6$ )                                           | 0.16 ( $\pm 0.05$ ) |
| DiolAX |        | 55 ( $\pm 5$ )                        | 57 ( $\pm 3$ )         | 60 ( $\pm 3$ )                                           | 0.70 ( $\pm 0.50$ ) |

(25%). Additionally, this methodology may also be useful for investigating the effects of other modification methods on the local chain mobility of polysaccharides.

### CRedit authorship contribution statement

**Ratchawit Janewithayapun:** Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Hampus Karlsson:** Writing – review & editing, Software, Methodology, Formal analysis, Conceptualization. **Mikael S. Hedenqvist:** Writing – review & editing, Supervision. **Dennis Wilkens Juhl:** Writing – review & editing, Resources, Methodology, Investigation. **Thomas Vosegaard:** Writing – review & editing, Software, Methodology, Formal analysis. **Lars Evenäs:** Writing – review & editing, Methodology. **Anna Ström:** Writing – review & editing, Supervision, Funding acquisition.

### Funding sources

We acknowledge the financial contribution from Formas – Swedish Research Council for Sustainable Development, with grant number 2020-01235.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Acknowledgments

We acknowledge access to NMR instrumentation at the Interdisciplinary Nanoscience Center, Aarhus University, through the PANACEA project funded by the European Union's Horizon 2020 research and innovation programme under grant agreement No 101008500. We acknowledge MAX IV Laboratory for time on beamline CoSAXS under Proposal 20221186 and 20231013. Research conducted at MAX IV, a Swedish national user facility, is supported by the Swedish Research Council under contract 2018-07152, the Swedish Governmental Agency for Innovation Systems under contract 2018-04969, and Formas under contract 2019-02496.

### Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.carbpol.2026.125873>. Supplementary information showing: monosaccharide composition and glycosidic linkage analysis results, SAXS data and fits, DVS isotherms, CP/MAS intensity buildup curves, 2D WISE plots of samples stored at 10% RH, and fits of WISE mobile component buildup with mixing time.

### Data availability

Data will be made available on a public repository upon publication at <https://doi.org/10.5281/zenodo.19210787>.

### References

- Amer, H., Nypelö, T., Sulaeva, I., Bacher, M., Henniges, U., Potthast, A., & Rosenau, T. (2016). Synthesis and characterization of periodate-oxidized polysaccharides: Dialdehyde Xylan (DAX). *Biomacromolecules*, 17(9), 2972–2980. <http://dx.doi.org/10.1021/acs.biomac.6b00777>.
- Bardet, M., Gerbaud, G., Tràn, Q.-K., & Hediger, S. (2007). Study of interactions between polyethylene glycol and archaeological wood components by  $^{13}\text{C}$  high-resolution solid-state CP-MAS NMR. *Journal of Archaeological Science*, 34(10), 1670–1676. <http://dx.doi.org/10.1016/j.jas.2006.12.005>.
- Börjesson, M., Larsson, A., Westman, G., & Ström, A. (2018). Periodate oxidation of xylan-based hemicelluloses and its effect on their thermal properties. *Carbohydrate Polymers*, 202, 280–287. <http://dx.doi.org/10.1016/j.carbpol.2018.08.110>.
- Börjesson, M., Westman, G., Larsson, A., & Ström, A. (2019). Thermoplastic and flexible films from arabinoxylan. *ACS Applied Polymer Materials*, 1(6), 1443–1450.
- Buist, G. J., Bunton, C. A., & Hipperson, W. C. P. (1971). The mechanism of oxidation of  $\alpha$ -glycols by periodic acid. Part X. The oxidation of pinacol, and a general discussion of the stability of periodate esters and their role in the mechanism of oxidation. *J. Chem. Soc. B*, 2128–2142. <http://dx.doi.org/10.1039/J29710002128>.
- Buist, G. J., Bunton, C. A., & Miles, J. H. (1959). 149. The mechanism of oxidation of  $\alpha$ -glycols by periodic acid. part V. Cyclohexane-1 : 2-diols. *J. Chem. Soc.*, 743–748. <http://dx.doi.org/10.1039/JR9590000743>.
- Guigo, N., Mazeau, K., Putaux, J.-L., & Heux, L. (2014). Surface modification of cellulose microfibrils by periodate oxidation and subsequent reductive amination with benzylamine: A topochemical study. *Cellulose*, 21(6), 4119–4133. <http://dx.doi.org/10.1007/s10570-014-0459-0>.
- Hodge, R. M., Bastow, T. J., Edward, G. H., Simon, G. P., & Hill, A. J. (1996). Free volume and the mechanism of plasticization in water-swollen poly(vinyl alcohol). *Macromolecules*, 29(25), 8137–8143. <http://dx.doi.org/10.1021/ma951073j>.
- Holland, G. P., Lewis, R. V., & Yarger, J. L. (2004). WISE NMR characterization of nanoscale heterogeneity and mobility in supercontracted nephila clavipes spider dragline silk. *Journal of the American Chemical Society*, 126(18), 5867–5872. <http://dx.doi.org/10.1021/ja031930w>.
- Jacob, D., & Falourd, X. (2025). Solid-State NMR Principles. <https://hal.inrae.fr/hal-05405099>. Fundamental principles of solid-state NMR, introducing concepts and principles to a scientific but non-expert audience in the field.
- Janewithayapun, R., Cousin, F., de Moura Pereira, P. F., Herranz-Trillo, F., Terry, A. E., Pedersen, J. S., Jiménez-Quero, A., & Ström, A. (2025). Correlation between arabinose content and the conformation of arabinoxylan in water dispersions. *Carbohydrate Polymers*, 368, Article 124082. <http://dx.doi.org/10.1016/j.carbpol.2025.124082>.
- Janewithayapun, R., Hedenqvist, M. S., Cousin, F., Idström, A., Evenäs, L., Lopez-Sanchez, P., Westman, G., Larsson, A., & Ström, A. (2024). Nanostructures of etherified arabinoxylans and the effect of arabinose content on material properties. *Carbohydrate Polymers*, 331, Article 121846. <http://dx.doi.org/10.1016/j.carbpol.2024.121846>.
- Janewithayapun, R., Karlsson, H., Herranz-Trillo, F., Terry, A. E., Evenäs, L., Cousin, F., & Ström, A. (2026). Effect of periodate oxidation and borohydride reduction on the chemical structure and chain conformation of arabinoxylan. *Carbohydrate Polymers*, 376, Article 124811. <http://dx.doi.org/10.1016/j.carbpol.2025.124811>.
- Jensen, A. B., Christensen, T. E. K., Weninger, C., & Birkedal, H. (2022). Very large-scale diffraction investigations enabled by a matrix-multiplication facilitated radial and azimuthal integration algorithm: MatFRAIA. *Journal of Synchrotron Radiation*, 29(6), 1420–1428.
- Juhl, D. W., Tošner, Z., & Vosegaard, T. (2020). Chapter one - versatile NMR simulations using SIMPSON. In G. A. Webb (Ed.), *Annual reports on NMR spectroscopy: Vol. 100, Annual reports on NMR spectroscopy* (pp. 1–59). Academic Press, <http://dx.doi.org/10.1016/bs.arnmr.2019.12.001>.
- Karlsson, H., Svenningsson, L., Storm, R., Chaiyupatham, P., Brodin, A., Larsson, A., Pinon, A. C., Schantz, S., Karlson, L., Larsson, P. A., et al. (2024). Dynamic nuclear polarization solid-state NMR spectroscopy as a tool to rapidly determine degree of modification in dialcohol cellulose. *Cellulose*, 31(18), 10727–10744.
- Kasai, W., Morooka, T., & Ek, M. (2014). Mechanical properties of films made from dialcohol cellulose prepared by homogeneous periodate oxidation. *Cellulose*, 21, 769–776.
- Kim, U.-J., Kuga, S., Wada, M., Okano, T., & Kondo, T. (2000). Periodate oxidation of crystalline cellulose. *Biomacromolecules*, 1(3), 488–492. <http://dx.doi.org/10.1021/bm0000337>.
- Koppe, J., Yakimov, A. V., Giofrè, D., Usteri, M.-E., Vosegaard, T., Pintacuda, G., Lesage, A., Pell, A. J., Mitchell, S., Pérez-Ramírez, J., & Copéret, C. (2025). Coordination environments of Pt single-atom catalysts from NMR signatures. *Nature*, 642(8068), 613–619. <http://dx.doi.org/10.1038/s41586-025-09068-x>.

- Kristiansen, K. A., Potthast, A., & Christensen, B. E. (2010). Periodate oxidation of polysaccharides for modification of chemical and physical properties. *Carbohydrate Research*, 345(10), 1264–1271. <http://dx.doi.org/10.1016/j.carres.2010.02.011>, Special Issue: Selected Papers from the 15th European Carbohydrate Symposium, Vienna 2009.
- Larsson, P. A., Berglund, L. A., & Wågberg, L. (2014). Ductile all-cellulose nanocomposite films fabricated from core-shell structured cellulose nanofibrils. *Biomacromolecules*, 15(6), 2218–2223. <http://dx.doi.org/10.1021/bm500360c>.
- Larsson, P. A., Gimåker, M., & Wågberg, L. (2008). The influence of periodate oxidation on the moisture sorptivity and dimensional stability of paper. *Cellulose*, 15, 837–847.
- Leguy, J., Diallo, A., Putaux, J. L., Nishiyama, Y., Heux, L., & Jean, B. (2018). Periodate oxidation followed by NaBH<sub>4</sub> reduction converts microfibrillated cellulose into sterically stabilized neutral cellulose nanocrystal suspensions. *Langmuir*, 34(37), 11066–11075. <http://dx.doi.org/10.1021/acs.langmuir.8b02202>.
- López Durán, V., Larsson, P. A., & Wågberg, L. (2016). On the relationship between fibre composition and material properties following periodate oxidation and borohydride reduction of lignocellulosic fibres. *Cellulose*, 23(6), 3495–3510. <http://dx.doi.org/10.1007/s10570-016-1061-4>.
- Lucia, A., Bacher, M., van Herwijnen, H. W. G., & Rosenau, T. (2020). A direct silanization protocol for dialdehyde cellulose. *Molecules*, 25(10), <http://dx.doi.org/10.3390/molecules25102458>.
- Maekawa, E., Kosaki, T., & Koshijima, T. (1986). Periodate oxidation of mercerized cellulose and regenerated cellulose. *Wood Research: Bulletin of the Wood Research Institute Kyoto University*, 73, 44–49.
- McBrierty, V. J., & Packer, K. J. (1993). Basic concepts in NMR. In *Cambridge solid state science series, Nuclear magnetic resonance in solid polymers* (pp. 16–50). Cambridge University Press.
- Mirau, P. A. (2004a). The dynamics of polymers. In *A practical guide to understanding the NMR of polymers* (pp. 359–396). John Wiley & Sons.
- Mirau, P. A. (2004b). Introduction to NMR. In *A practical guide to understanding the NMR of polymers* (pp. 66–77). John Wiley & Sons.
- Morooka, T., Norimoto, M., & Yamada, T. (1989). Periodate oxidation of cellulose by homogeneous reaction. *Journal of Applied Polymer Science*, 38(5), 849–858. <http://dx.doi.org/10.1002/app.1989.070380508>.
- Münster, L., Vicha, J., Kľofáč, J., Masař, M., Kucharczyk, P., & Kuřitka, I. (2017). Stability and aging of solubilized dialdehyde cellulose. *Cellulose*, 24, 2753–2766.
- Painter, T. J. (1988). Control of depolymerisation during the preparation of reduced dialdehyde cellulose. *Carbohydrate Research*, 179, 259–268. [http://dx.doi.org/10.1016/0008-6215\(88\)84123-5](http://dx.doi.org/10.1016/0008-6215(88)84123-5).
- Palasingh, C., Ström, A., Amer, H., & Nypelö, T. (2021). Oxidized xylan additive for nanocellulose films – A swelling modifier. *International Journal of Biological Macromolecules*, 180, 753–759. <http://dx.doi.org/10.1016/j.ijbiomac.2021.03.062>.
- Pedersen, J. S., & Schurtenberger, P. (1996). Scattering functions of semiflexible polymers with and without excluded volume effects. *Macromolecules*, 29(23), 7602–7612.
- Pedersen, J. S., & Schurtenberger, P. (2004). Scattering functions of semidilute solutions of polymers in a good solvent. *Journal of Polymer Science Part B: Polymer Physics*, 42(17), 3081–3094.
- Pettolino, F. A., Walsh, C., Fincher, G. B., & Bacic, A. (2012). Determining the polysaccharide composition of plant cell walls. *Nature Protocols*, 7(9), 1590–1607.
- Plappert, S. F., Quraishi, S., Pircher, N., Mikkonen, K. S., Veigel, S., Klinger, K. M., Potthast, A., Rosenau, T., & Liebner, F. W. (2018). Transparent, flexible, and strong 2,3-dialdehyde cellulose films with high oxygen barrier properties. *Biomacromolecules*, 19(7), 2969–2978. <http://dx.doi.org/10.1021/acs.biomac.8b00536>.
- Potthast, A., Kostic, M., Schiehser, S., Kosma, P., & Rosenau, T. (2007). Studies on oxidative modifications of cellulose in the periodate system: Molecular weight distribution and carbonyl group profiles. *Holzforschung*, 61(6), 662–667. <http://dx.doi.org/10.1515/HF.2007.099>.
- Radloff, D., Boeffel, C., & Spiess, H. W. (1996). Cellulose and cellulose/poly(vinyl alcohol) blends. 2. Water organization revealed by solid-state NMR spectroscopy. *Macromolecules*, 29(5), 1528–1534. <http://dx.doi.org/10.1021/ma950405h>.
- Salmén, L., & Larsson, P. A. (2018). On the origin of sorption hysteresis in cellulosic materials. *Carbohydrate Polymers*, 182, 15–20. <http://dx.doi.org/10.1016/j.carbpol.2017.11.005>.
- Schmidt-Rohr, K., Clauss, J., & Spiess, H. W. (1992). Correlation of structure, mobility, and morphological information in heterogeneous polymer materials by two-dimensional wideline-separation nmr spectroscopy. *Macromolecules*, 25(12), 3273–3277. <http://dx.doi.org/10.1021/ma00038a037>.
- Simon, J., Schlapp-Hackl, I., Sapkota, J., Ristolainen, M., Rosenau, T., & Potthast, A. (2024). Towards tailored dialdehyde cellulose derivatives: A strategy for tuning the glass transition temperature. *ChemSusChem*, 17(5), Article e202300791. <http://dx.doi.org/10.1002/cssc.202300791>.
- Virtanen, P., Gommers, R., Oliphant, T. E., Haberland, M., Reddy, T., Cournapeau, D., Burovski, E., Peterson, P., Weckesser, W., Bright, J., van der Walt, S. J., Brett, M., Wilson, J., Millman, K. J., Mayorov, N., Nelson, A. R. J., Jones, E., Kern, R., Larson, E., .... SciPy 1.0 Contributors (2020). SciPy 1.0: Fundamental algorithms for scientific computing in python. *Nature Methods*, 17, 261–272. <http://dx.doi.org/10.1038/s41592-019-0686-2>.
- Voelkel, R. (1988). High-resolution solid-state <sup>13</sup>C-NMR spectroscopy of polymers [new analytical methods (37)]. *Angewandte Chemie International Edition in English*, 27(11), 1468–1483. <http://dx.doi.org/10.1002/anie.198814681>.
- Vold, I. M. N., Kristiansen, K. A., & Christensen, B. E. (2006). A study of the chain stiffness and extension of alginates, in vitro epimerized alginates, and periodate-oxidized alginates using size-exclusion chromatography combined with light scattering and viscosity detectors. *Biomacromolecules*, 7(7), 2136–2146. <http://dx.doi.org/10.1021/bm060099n>.