Investigation of Starch Hydration by 2D Time Domain NMR

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Proton exchange between spin groups of the solid matrix of hydrated granular potato starch and water was studied using the 2D time domain NMR. The proton spin–spin relaxation time T_2, and spin–lattice relaxation time T_1 (selective and non-selective pulse sequences) were measured at room temperature. The observed spin relaxation results were analysed for exchange assuming a two-site exchange model (between water and solid matrix of starch). In this analysis we determined the intrinsic spin–lattice relaxation time for water protons (49 ms) and solid starch matrix protons (172 ms), as well as the water–starch magnetization exchange rate (86 s^{-1}).

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1. Introduction

The structure of native starch granules was studied using a variety of microscopic and scattering techniques, including optical, electron, and atomic force microscopy, light, X-ray, and neutron scattering [1–4]. The physical and structural properties of starch are strongly dependent on molecular interactions with water. NMR is an excellent technique for studying the state of water and its dynamic behaviour in polymeric materials [5, 6]. In this paper, we report on a NMR investigation of the coupling between starch and water proton magnetizations in low hydrated starch sample.

2. Materials and methods

Granular potato starch, isolated in Nowamyl (Łobez, Poland) according to Polish Standard PN-A-74710, was dried in vacuum (10^{-3} Torr), at 105°C, for 24 h (dry sample). The potato starch hydrated sample was prepared by exposing the

dry sample to 100% humidity in a glass desiccator for two days. The moisture content (MC) was 10.6%, calculated as the weight of water relative to the dry wood weight, expressed in percent.

The measurements of T_1 and T_2 were performed using a pulsed WNS HB-65 NMR spectrometer working at 30 MHz. T_2 was obtained from the free-induction decay (FID), following a short (1.7 μs) 90° RF pulse. T_1 was measured using two different pulse sequences: non-selective standard inversion recovery sequence (hard–hard T_1), and the selective inversion recovery sequence (soft–hard T_1) with a soft 180° pulse. The non-selective inversion recovery sequence $(180° - \tau - 90°)$ uses short (time duration = 1.7 μs $\ll T_2$) pulses, or "hard" pulses, which invert all protons. In the selective sequence a low power 180° pulse, applied for 60 μs (a time greater than T_2 of the solid component magnetization), also called a "soft" pulse, is followed by a hard 90° monitoring pulse. The soft 180° pulse is only effective in inverting the water component magnetization. The second pulse rotates the total magnetization into the $x-y$ plane for detection. During the time τ, Zeeman magnetization may exchange between spin groups. If the exchange rate is fast on the T_1 time scale a single T_1 is observed [7].

The 2D time domain NMR technique ([8, 9] and references therein) was applied in the T_1 experiments. In this approach the data are acquired along the t (FID time axis) and the τ axis, and stored in a 2D matrix with the indices representing the two time axes. Thus, for each value of t a magnetization recovery curve is stored. The magnetization recovery curves at all values of t were then simultaneously fit to a single exponential (for the hard–hard T_1 experiment) or a double exponential (for the soft–hard T_1 experiment) using the Marquardt non--linear least squares fitting algorithm. Such analysis of the 2D data set yields a T_1 for the single exponential case, and two T_1 values for the double exponential case. The $\tau = 0$ intercepts, obtained from the fit for all t values, are used to reconstruct a FID. By fitting the reconstructed FID to an appropriate FID function (Gaussian damped sinc for dry starch and a sum of Gaussian damped sinc and exponential for the hydrated starch) the apparent magnetization fractions (from the $t = 0$ intercepts), and T_2 values of spin groups distinguished by values of T_1 are obtained.

3. Results and discussion

The FID for the hydrated sample of starch is shown in Fig. 1. In keeping with previous work [10] the presence of the small oscillation in the solid component of the FID prompts us to fit this component to a Gaussian damped sinc function. The liquid-like signal was modelled as an exponential so that the FID in the hydrated sample becomes,

$$F_s(t) = f_{\mathrm{S}} \exp\left(-\left(\frac{t}{T_{2\mathrm{G}}}\right)^2\right) \frac{\sin(at)}{at} + f_L \exp\left(-\frac{t}{T_{2E}}\right), \tag{0}$$

where f_{S} is the magnetization of the solid component, $T_{2\mathrm{G}}$ is the spin–spin relaxation time associated with the Gaussian damping factor, a is a constant, f_L is the
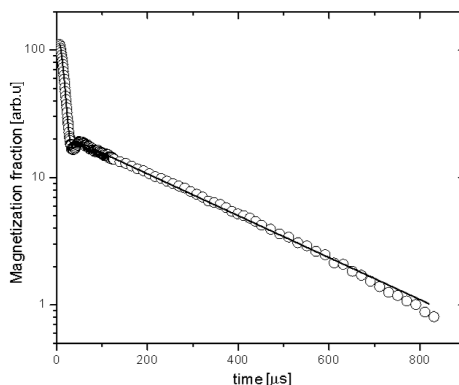
Fig. 1.   Proton FID in the hydrated potato starch sample with MC = 10.6%. The solid line was calculated from Eq. (0) with fitted T_2 values and magnetization fractions given in Table.

TABLE

The observed relaxation parameters of potato starch sample hydrated to 10.6%.

T_2 FID	Fraction [%]	82.2	17.8		
	T_2 [μs]	22.0 ± 0.2	264 ± 2		
hard–hard T_1	Fraction [%]	82.5	17.5		
	T_2 [μs]	22.4 ± 0.3	268 ± 5		
	T_1 [ms]	122 ± 3			
soft–hard T_1	Fraction [%]	(-)16.2	18.2	80.6	17.4
	T_2 [μs]	21.7 ± 1	296 ± 4	22.9 ± 0.4	252 ± 5
	T_1 [ms]	2.00 ± 0.04		120 ± 3	

magnetization of the exponential component, and T_{2E} is its spin–spin relaxation time. The solid line (Fig. 1) was calculated from Eq. (0), with the T_2 values and normalized magnetization fractions, obtained from the fit, given in Table. It may be noted that the T_2 values obtained from the present fit of the Gaussian damped sinc function or sinc-Gaussian function (~ 20 μs) (Eq. (0)) are longer than those observed for the Gaussian fit for biological dry matrices (~ 14 μs) [8].

For the dry starch sample the main part of the FID (not shown) is well described by the sinc-Gaussian function with $T_{2G} = (21.1 \pm 0.1)$ μs. Therefore, in the FID of the hydrated sample the solid-like signal (82.2% of the signal), described by the sinc-Gaussian with $T_{2G} = (22.0 \pm 0.2)$ μs, was assigned to polymer protons. The remaining 17.8% of the signal with T_{2E} equal to (264 ± 2) μs, can be associated with protons of water.

In the analysis of the recovery curves from the hard–hard T_1 experiment a single T_1 was fitted. 2D time evolution analysis of these results yielded two

reconstructed FIDs with the values of T_2 and fractions similar to those found in the FID experiments (Table). The fact that the magnetizations with liquid-like and solid-like T_2's exhibit the same value of T_1 shows that the exchange couples the spin–lattice relaxations of these two spin groups strongly enough to produce the single T_1.

More information about this system is obtained from the selective soft–hard T_1 experiment, in which we resolve two component magnetizations. The T_1 values and reconstructed FIDs obtained from the 2D analysis are shown in Fig. 2a and b, respectively. The component magnetization T_1 values averaged over all time windows, the normalized magnetization fractions, and the reconstructed FID T_2 values are given in Table. The negative signal with short T_1 seen in the reconstructed FID (Fig. 2b) indicates the presence of magnetization exchange between solid-like and liquid-like spin groups.
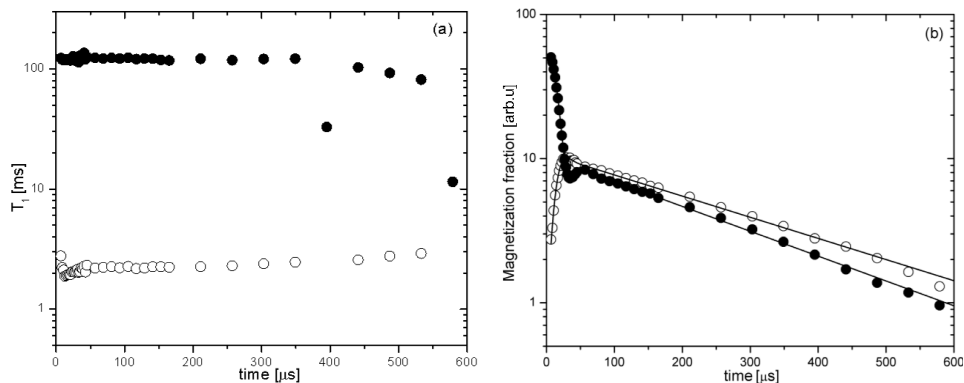

Fig. 2.   Results of 2D time domain NMR experiment using the soft–hard T_1 sequence in hydrated potato starch sample at 30 MHz. (a) Variation of T_1 as a function of time window along FID: the magnetization recovery is characterized by two time constants (T_1's) equal to (2.00 ± 0.04) ms and (120 ± 3) ms at all windows, (b) the reconstructed FIDs corresponding to the two component T_1's shown in (a).

The results in the hydrated potato starch sample have been interpreted in terms of a two-site exchange model, where the two sites correspond to the starch and water magnetization reservoirs. Letting the reduced magnetization of reservoir i equal $m_i(\tau) = (M_{0i} - M_i(\tau))/2M_{0i}$, its evolution in time within the two-site exchange model may be written,

$$\frac{\mathrm{d}m_i(\tau)}{\mathrm{d}\tau} = -\left[\left(\frac{1}{T_{1,\mathrm{int}}}\right)_i + k_{ij}\right] m_i(\tau) + k_{ij}m_j(\tau), \tag{1}$$

where $(i,\ j) = $ (starch, water), $(1/T_{1,\mathrm{int}})_i$ is the intrinsic relaxation rate of the ith reservoir magnetization, and k_{ij} is the rate of magnetization transfer from the ith to the jth reservoir. The solution of Eq. (1) has the following form:

$$m_i(\tau) = C_i^- \exp\left(-\left(\frac{1}{T_{1,\mathrm{app}}}\right)^- \tau\right) + C_i^+ \exp\left(-\left(\frac{1}{T_{1,\mathrm{app}}}\right)^+ \tau\right), \qquad (2)$$

where the $(1/T_{1,\mathrm{app}})^\pm$'s are the apparent relaxation rates, and the $C_i^\pm$'s are apparent magnetization fractions, which are a function of the $(1/T_{1,\mathrm{int}})_{i[j]}$'s, k_{ij}'s, intrinsic magnetization fractions, and effect of the preparation pulse in the inversion recovery sequence. The relations between apparent and intrinsic parameters are given by

$$\left(\frac{1}{T_{1,\mathrm{app}}}\right)^\pm = \frac{1}{2}\Bigg\{ \left(\frac{1}{T_{1,\mathrm{int}}}\right)_i + \left(\frac{1}{T_{1,\mathrm{int}}}\right)_j + k_{ij} + k_{ji}$$

$$\pm \sqrt{\left[\left(\frac{1}{T_{1,\mathrm{int}}}\right)_i - \left(\frac{1}{T_{1,\mathrm{int}}}\right)_j + k_{ij} - k_{ji}\right]^2 + 4k_{ij}k_{ji}}\Bigg\},$$

$$C_{i[j]}^\pm = \pm \frac{m_{i[j]}(0)}{\left[\left(\frac{1}{T_{1,\mathrm{app}}}\right)^+ - \left(\frac{1}{T_{1,\mathrm{app}}}\right)^-\right]}$$

$$\times \left[\left(\frac{1}{T_{1,\mathrm{int}}}\right)_{i[j]} - \left(\frac{1}{T_{1,\mathrm{app}}}\right)^\mp + \left(1 - \frac{m_{j[i]}(0)}{m_{i[j]}(0)}\right) k_{ij[ji]}\right], \qquad (3)$$

where $m_{i[j]}(0)$ are the reduced magnetizations of spins in the ith or jth site prior to period τ.

In the experiment, the values of the magnetization fractions (values of $C_{i[j]}^\pm$ in the model) are found from the reconstructed FIDs as shown in Fig. 2b (the values of parameters are given in Table). The experimental parameters, and model apparent parameters calculated from Eq. (3) for certain trial intrinsic values of these parameters are compared within an iterative minimization algorithm, giving the intrinsic relaxation parameters $((1/T_{1,\mathrm{int}})_{i[j]}$ and $k_{ij})$, which represent the best match between these two sets of parameters [8]. We found the exchange rate $k_{\mathrm{starch-water}} = 86 \mathrm{\ s}^{-1}$, and spin–lattice relaxation time $T_{1\mathrm{starch}} = 172$ ms for the major 82.2% component, and $T_{1\mathrm{water}} = 49$ ms for the minor 17.8% component magnetization. It is seen that the obtained exchange rate is fast enough to satisfy the fast exchange condition, consistent with the observation of single-exponential T_1 in the hard–hard experiment.

The native potato starch granules are composed mainly of two glucose polymers: linear amylose and highly branched amylopectin. The molecular structure of native potato starch granules includes semi-crystalline layers (mainly built from amylopectin), which are separated by amorphous regions (built from amylose and branched points of amylopectin). The hydroxyl groups (OH) of glucose units of starch polymers are accessible to water [3]. For the present low hydration sample of native potato starch we assign the exchange process, quantified through

$k_{\text{starch}-\text{water}}$, to chemical exchange of protons of water molecules with protons of hydroxyl groups of the amylopectin and amylose molecules on the surface of the granule.

4. Conclusion

2D time domain NMR results in hydrated starch were used in a two-site exchange model to analyse exchange between protons of the solid starch matrix and protons of water molecules. The exchange rate (86 s^{-1}) found from this analysis clearly indicates that magnetization exchange plays an important role in controlling the observed spin–lattice relaxation in hydrated starch. Thus, any meaningful analysis of NMR spin–lattice relaxation data for water molecule dynamics in this material must include a careful consideration of magnetization exchange effects.

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