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Solid-like components in carbohydrate gels probed by NMR spectroscopy

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Abstract

Solid-like components in maltodextrin and inulin model gels were probed with NMR spectroscopy. ^1H NMR cross-relaxation experiments yielded quantitative information about the ageing process during which the immobile fraction of the polymer increased. The increase of immobile protons was correlated with crystallization in the gels. From the growth rate of the amount of solid-like component in inulin and maltodextrin gels different kinetics of ageing were deduced. In the case of inulin, the fraction of immobilized polymer was reduced at lower polymer concentration which was correlated with the observed decrease in the gel strength. Firming of the inulin gel took longer when starting from totally dissolved polysaccharide material, as was the case with solutions prepared at temperatures exceeding 82°C. However, neither the kinetics of solidification, nor the fraction of immobilized polymer at equilibrium appeared to be influenced by the temperature at which the starting solution had been prepared. Additionally, molecular mobility of maltodextrin chains and interaction with water in the gel was investigated by ^{13}C 1D and 2D solid-state NMR. The molecular mobility of the polymer chains was studied as a function of storage time and storage temperature and turned out to be higher in gels stored at higher temperatures. Water binding was probed with the WISE experiment. Lower molecular mobility of polysaccharide chains as well as stronger interaction with water in gels stored at lower temperature was attributed to the formation of a 3D polymer network accompanied by partial crystallization. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Carbohydrate gels; Maltodextrin; NMR spectroscopy; Inulin

1. Introduction

Many polysaccharides when added to water can mimic the function of fats by stabilizing substantial quantities of water in a gel-like matrix, resulting in lubricant and flow properties similar to those of fats. The current technology used in carbohydrate-based fat replacers stems from early work of Richter, Schierbaum, Augustat and Knock (1976a,b), who first described the preparation and properties of a low DE (dextrose equivalent) potato-based maltodextrin. This product forms a white, glossy, thermo-reversible gel when dispersed in water. Presently, mechanistic insight into carbohydrate gel structure formation at the molecular level is still insufficient to fully understand its relationship with the functional behavior of food systems based on these gels.

The process of ageing in starch-type polysaccharide/water systems has previously been studied using a variety of physico-chemical methods (Reuther et al., 1984; Miles, Morris & Ring, 1985; Bulkin, Kwak & Dea, 1987; Russel, 1987; Biliaderis & Zawistowski, 1990; Fannon & BeMiller, 1992; Schierbaum, Radosta, Vorwerg, Yuriev, Braudo & German, 1992). The molecular picture emerging from these studies is that during ageing there is initially a first transition from a disordered state (random coil) to an ordered, helical conformation. This process is followed by the formation of a physically crosslinked network at the superhelical level (Viebeke, Piculell & Nilsson, 1994). Regardless of the mechanism of polysaccharide gel formation, the development of gel-like rheological properties in such systems is accompanied by the appearance of a fraction of immobilized carbohydrate material. One of the objectives in research on polysaccharide gels is to quantify these immobilized fractions, and to relate them to the physico-chemical properties of the material and one of the most powerful techniques that can be used is NMR.

It has been shown that cross-relaxation NMR spectroscopy (Grad & Bryant, 1990) can be successfully employed to achieve this (Wu, Bryant & Eads, 1992). This technique can selectively detect solid-like domains in aqueous gels, by monitoring the response of the H_2O NMR signal upon saturation of the immobilized carbohydrate material by low-power irradiation. Thus, the line shape can be obtained of rigidified phases in aqueous matrices. This technique was successfully applied in a variety of investigations on

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biopolymeric materials (Wolff & Balaban, 1989; Grad & Bryant, 1990; Wu et al., 1992; Ni & Eads, 1993; Wu & Eads, 1993). However, only few attempts (Henkelman, Huang Xian, Stanisz, Swanson & Bronskill, 1993; Tessier, Dillon, Carpenter & Hall, 1995; Degrassi, Toffanin, Paoletti & Hall, 1998) have been made to extract quantitative information from cross-relaxation data, in terms of the molecular mobility and amount of the rigidified phase (we note in passing that in the latter three references, the cross-relaxation NMR technique is also referred to as "magnetization transfer" spectroscopy).

Solid-state NMR has proved to be a successful technique in characterizing the local molecular structure, conformational order and dynamics in polymers (Schmidt-Rohr & Spiess, 1994). The most important advantage of this technique is its selectivity, yielding high resolution in particular of ^{13}C nuclei at natural abundance. This is achieved by a combination of cross-polarization (CP) (Pines, Gibby & Waugh, 1973) and magic-angle spinning (MAS) (Schaefer & Stejskal, 1976). ^{13}C CP-MAS spectra yield structural information through well-separated isotropic chemical shifts and have been used to determine the degree of molecular ordering in starch granules (Gidley, 1992).

Molecular mobility, domain formation and interaction between polysaccharide chains and water can be investigated by measuring proton rotating-frame relaxation times $T_{1\rho}$ (^{1}H). The $T_{1\rho}$ (^{1}H) experiment is commonly performed by monitoring the intensity of ^{13}C NMR signals as a function of the duration of a ^{1}H spinlock field. In this manner the structural specificity of the ^{13}C NMR spectrum is combined with the dynamic information comprised in the $T_{1\rho}$ (^{1}H) values. These $T_{1\rho}$ (^{1}H) values are sensitive to kHz-regime motions of polymer chains, and have been used extensively to characterize motions in polymers (Stejskal, Schaefer & Steger, 1979). Likewise, local dynamics in carbohydrate chains can be probed by recording ^{1}H NMR widelines. The width of the ^{1}H NMR line characterizes the strength of the dipolar coupling between protons and yields information about the molecular mobility in the tens of kHz-regime. One obvious shortcoming of ^{1}H NMR widelines, however, is the lack of structural specificity due to severe signal overlap. In addition, highly hydrated materials, like gels, also produce ^{1}H NMR widelines that are dominated by a large H_2O signal, thus hampering observation of the lineshape of the rigidified phase. Both disadvantages can be circumvented by combining the concepts of probing molecular mobility by ^{1}H wideline spectra and chemical structure by ^{13}C CP-MAS in a heteronuclear two-dimensional (2D) wideline separation experiment (WISE-NMR) (Schmidt-Rohr, Clauss & Spiess, 1992; Tekely, Palmas & Mutzenhardt, 1993). In this experiment the chemical structure is reflected by the signals along the ^{13}C chemical shift axis whereas for each of the ^{13}C signals, a corresponding ^{1}H wideline is obtained indicating the local mobility at the specific chemical position. The WISE experiment can be used to probe the contact between water and the polymer matrix (Ganapathy, Rajamohanan, Ray, Mandhare & Mashelkar, 1994; Kulik, de Costa & Haverkamp, 1994), thus providing information which is not obtainable with 1D NMR spectroscopy.

Maltodextrin gels have previously been studied with a variety of NMR techniques (German, Blumenfeld, Yuryev & Tostoguzov, 1989; Mora-Guitierrez & Baianu, 1990, 1991; Schierbaum et al., 1992). ^{1}H, ^{2}H and ^{17}O NMR transverse relaxation measurements were used to probe both chemical exchange with the solvent and hydrogen bonding involving hydroxyl groups. On the basis of those measurements it was suggested that gelation involves the formation of a stable molecular network. Apparently, water is highly mobile in hydrated maltodextrin and contributes little to the stability of the gel. ^{13}C NMR studies revealed differences in the degree of cross-linking as well as in the gelling properties of maltodextrins. Another food-grade carbohydrate material which can be used for water phase structuring is inulin. To our knowledge no NMR reports on structure formation of inulin gels have yet been published. Earlier studies (Phelps, 1965) suggest that the structure formation in inulin gels takes place in a way similar to that in maltodextrin gels.

The aim of the present work has been to investigate the applicability of the advanced solid-state NMR methods mentioned above to obtain information on the structure and mobility in maltodextrin and inulin model gels. Such information can then be used to characterize and quantify physico-chemical processes and properties of the gels.

2. Experimental methods

2.1. Sample preparation

Maltodextrin (Paselli SA 2) and inulin (Raftaline) were obtained from AVEBE (Foxhol, The Netherlands) and from Tienense Suikerraffinaderij (Tienen, Belgium), respectively. Samples were of commercial grade and were used without any chemical treatment. Paselli SA2 is an enzymatically converted potato starch with DE < 3. Inulin is a fructan obtained from chicory. The average degree of polymerization is 10. Gels were prepared from 30 or 35% (w/w) of polysaccharide in water. The maltodextrin gel was prepared at 95°C; the inulin gels at 60°C and 85°C, respectively. The polysaccharide dispersions were agitated in an Ultraturrax mixer for 2 min., poured into NMR tubes and immediately measured. Aged maltodextrin samples were measured after: 1 day storage at 15°C (HT gel); 28 days storage at 15°C; and 1 day storage at 15°C followed by 28 days at −26°C and 1 day at 15°C (LT gel).

2.2. NMR experiments

All NMR experiments were performed at ambient temperature (20°C), on Bruker MSL-300 and DSX300 spectrometers operating at resonance frequencies of 75.47 and

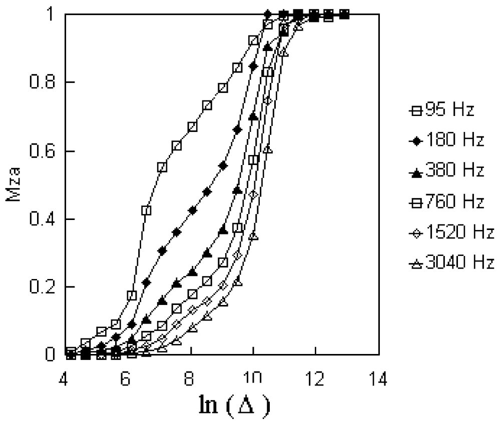

Fig. 1. Cross-relaxation data of a maltodextrin gel (30%) as a function of radiofrequency field strenght, ω, obtained 40 h after preparation (storage at room temperature, 20°C). On the horizontal axis the offset frequency of the irradiation field is plotted, the vertical axis depicts the fraction of the observed residual water resonance $M_{za}(\omega, \Delta)/M_{za}(0, 0)$.

300.13 MHz for ^{13}C and ^{1}H, respectively. For the cross-relaxation experiments, the preparation pulse was 3000 ms (radio frequency strengths ranged from 95 to 3040 Hz) and was applied with irradiation frequency offsets varying from 0 to 200 kHz. Typically, four transients with a repetition time of 5 s were averaged.

Proton rotating-frame relaxation times, $T_{1\rho}$ (^{1}H), were determined from the decay of the carbon signal as a function of ^{13}C–^{1}H contact time (τ) in a CP-MAS experiment (Stejskal et al., 1979). For these MAS experiments, the dry samples were spun at 5 kHz and gel/hydrated samples at 2 kHz in a variable-temperature double-resonance probe. The ^{1}H relaxation experiment was performed in this way to take advantage of the spectral resolution in ^{13}C NMR. The value of $T_{1\rho}$ (^{1}H) was calculated from a straight-line fit of log (carbon signal intensity) versus τ, where τ varied from 1 to 45 ms. The 2D WISE (Schmidt-Rohr et al., 1992; Tekely et al., 1993) spectra were obtained with a 1 ms cross-polarization time. The spectral width in the ^{1}H dimension was 100 kHz:, a dwell time of 10 μs was incremented at least 56 times. The ^{1}H 90° pulse in solid-state experiments was 4.5 μs. Between 1000 and 1500 transients were averaged with a repetition time of 1 s.

Data-analysis was performed using the PV-Wave (Visual Numerics, Inc.) and XWINNMR (Bruker) packages, both running at Silicon Graphics workstations.

2.3. Quantitative interpretation of cross-relaxation spectra

The magnetization transfer phenomena occurring during the cross-relaxation experiment can be described in detail by solving the Bloch equations for a system consisting of a liquid (M_a) and a solid (M_b) spin pool. The magnetizations of these spin pools (M_{za} and M_{zb}, respectively) can exchange via hydration and proton exchange, characterized by a singe parameter, R_{ab}. At prolonged irradiation times, a steady state will be reached and the following solution of the Bloch equations can be obtained (Grad & Bryant, 1990; Wu, 1991; Henkelman et al., 1993):

$$M_{za} = \frac{R_a(R_b + R_{ab} + R_{fb}) + R_b R_{ab} M_b}{(R_a + R_{ab} M_b + R_{fa})(R_b + R_{ab} + R_{fb}) R_{ab}^2 M_b}. \qquad (1)$$

Here R_{fa} and R_{fb} are the line shapes of the liquid (transverse relaxation time T_{2a}) and solid (transverse relaxation time T_{2b}) pools, under the perturbation of a rf-field with power ω and irradiation offset Δ:

$$R_{fa} = \frac{\omega^2 T_{2a}}{(1 + (2\pi\Delta T_{2a})^2)} \qquad (2)$$

$$R_{fb} = \omega^2 T_{2b}\sqrt{\frac{\pi}{2}\exp(-2\pi^2\Delta^2 T_{2b}^2)}. \qquad (3)$$

The (cross-)relaxation parameters (T_{2a}, T_{2b}, R_{ab} etc.) can be obtained by fitting Eq. (1) to cross-relaxation data. It has been found that these parameters can only be obtained if $M_{za}(\Delta, \omega)$ is measured as a function of both ω and Δ (Henkelman et al., 1993). In this report, $M_{za}(\Delta, \omega)$ datasets were fitted to Eq. (1) by Simplex and/or Marquardt minimization procedures (Press, Flannery, Teukolski & Vetterling, 1989). The errors for the fitted parameters were extracted from the square roots of the diagonal elements of the covariance matrix.

2.4. Semi-quantitative interpretation of cross-relaxation and WISE line shapes

In this study also cross-relaxation data $M_{za}(\Delta)$ have been obtained, where Δ was varied and the irradiation power level ω was kept fixed. Such a limited dataset does not render itself for fitting to the two-pool model Eq. (1), with its relatively large number of parameters. However, it has been shown that $M_{za}(\Delta)$ datasets can be deconvoluted into a (liquid) Lorentzian (f_L) and a (solid) Gaussian (f_G) contribution (Grad & Bryant, 1990; Wu, 1991):

$$M_{za}(\Delta) = (1 - \theta) \times f_L(\Delta) + \theta \times f_G(\Delta). \qquad (4)$$

The contribution (θ) of the Gaussian line shape to the total signal M_{za} is a function of both longitudinal (R_a, R_b) and cross-relaxation (R_{ab}) rates and abundance of the relative magnetizations (M_a and M_b) (vide supra). Unless prior knowledge exists on one of these parameters, the quantity θ can only be used as a semi-quantitative measure for the presence of a solid pool (b).

In a similar approach, also the ^{1}H NMR line shapes $f(\omega)$ which can be observed in a WISE experiment, can be deconvoluted in a Gaussian (f_G) and Lorentzian (f_L) line shape:

$$f(\omega) = (1 - \Phi) \times f_L(\omega) + \Phi \times f_G(\omega). \qquad (5)$$

The value $(1 - \Phi)/\Phi$ can be considered as a semi-quantitative measure for the contact between the solid carbohydrate phase (Gaussian) and water (Lorentzian).

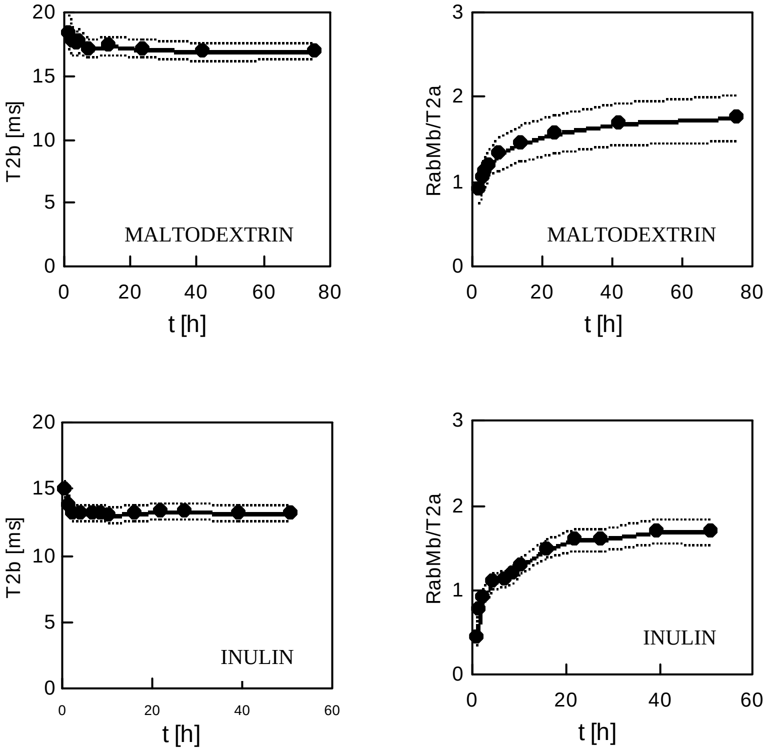

Fig. 2. Evolution of $R_{ab}M_b/T_{2a}$ (right) and T_{2b} (left) during ageing of (top) maltodextrin (30%) and (bottom) inulin (30%) gels. The parameters were obtained by fitting cross-relaxation data to a two-pool model (Eq. (1), see text). The dotted lines indicate the 95% confidence levels.

3. Results and discussion

3.1. Cross-relaxation spectra of maltodextrin and inulin gels

In order to monitor the kinetics of maltodextrin and inulin gel ageing, cross-relaxation spectra $M_{za}(\Delta, \omega)$ were recorded, where both irradiation frequency Δ and field strength ω were varied. Fig. 1 shows a cross-relaxation dataset obtained for a 30% maltodextrin gel. We have chosen to invoke a simple two-pool model, consisting of a rigid and a mobile phase, the latter consisting of water and dissolved carbohydrate polymer. It has been pointed out (Henkelman et al., 1993) that even for a simple two-pool model, cross-relaxation data obtained under "steady state" conditions can only yield relative values for most (cross-) relaxation parameters. However, the maltodextrin and inulin data were of sufficient quality to obtain quantitative values for T_{2b} and $R_{ab}M_b/T_{2a}$ by fitting the data to a two-pool magnetization model (see Section 2). The T_{2b} parameter is the transverse relaxation parameter of the solid pool and is proportional to its molecular mobility. The composite $R_{ab}M_b/T_{2a}$ parameter is composed of the cross-relaxation parameter R_{ab}, the solid phase proton abundance M_b and the transverse relaxation time of the mobile pool T_{2a}. The product $R_{ab}M_b$ is the amount of magnetization that can be transferred from the solid matrix to the liquid phase and is a measure for the abundance of the solid phase. In case of rigid phase formation, the T_{2a} parameter will most likely decrease due to surface relaxation of water on the solidified polymer. Hence, the $R_{ab}M_b/T_{2a}$ parameter is directly proportional to formation of a solidified phase. In Fig. 2 the (cross-)relaxation parameters and their confidence intervals, are shown for the 30% inulin and maltodextrin gels, as a function of gel ageing. The figure shows that the two (cross-)relaxation parameters could be obtained with an accuracy that is sufficient to monitor them during the growth of solid-like components in these gels (vide infra).

3.2. Increase of solid-like fraction in gels during ageing

For both the maltodextrin and inulin gels, the short values (17 and 14 μs, respectively) for the transverse relaxation time of the solid pool (T_{2b}), are indicative for a fairly rigid solid lattice present in the gel. Thus, in both cases the polymer chains are strongly immobilized. As mentioned in the Introduction, this can be attributed to the formation of a crosslinked network at the superhelical level (Viebeke et al., 1994). The short value for T_{2b} is already observed early (< 1 h) in the ageing process, indicating that a highly rigidified phase must be present at short time stages for both the maltodextrin and the inulin systems. The molecular mobility of this phase does not evolve much during the ageing process. In contrast to the relatively small effect on the T_{2b} parameter, a large increase can be observed for the $R_{ab}M_b/T_{2a}$ parameter (combination), during the ageing

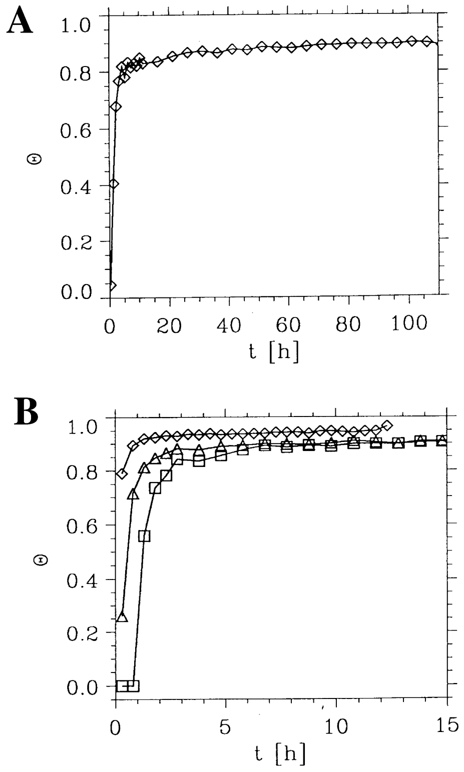

Fig. 3. Time-dependence of line shape ratio of cross-relaxation spectra of (A) maltodextrin gel (30%) at 20°C and of (B) inulin gels (30%) prepared at 85°C (□); 30% gel prepared at 60°C (△); 35% gel prepared at 60°C (◇)).

process, for both inulin and maltodextrin. This can be attributed to an increase of the abundance of the rigid polymer. The formation of the solid structures in the gel was verified by wide-angle X-ray scattering, revealing crystallinity which is in full agreement with earlier reported measurements (Schierbaum et al., 1992). Thus, the solid-like component detected in our measurements is correlated with the long-range ordering found by X-ray measurements revealing the crystalline fraction.

In order to monitor the formation of solid-like components with a higher time resolution, also cross-relaxation data were acquired with a single irradiation power level ω, ($M_{za}(\Delta)$ measured as a function of Δ), which requires only a few minutes. A measure for the amount of solidified material was obtained by fitting the data to a Lorenztian (mobile) and Gaussian (rigid) lines shape, f_L and f_G, respectively. The contribution of f_G, θ, to the total $M_{za}(\Delta)$ line shape is determined by the amount of solid material present. The experiments performed previously, demonstrated that mobility of the rigid polymer (inversely proportional to T_{2b}) was invariant during the ageing process. Hence, we can exclude that a change in θ is due to a change in mobility of the solid fraction. Thus, θ can be employed to monitor the kinetics of solid phase formation.

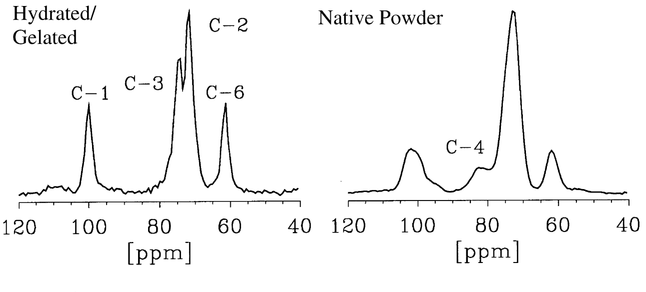

Fig. 4. ^{13}C CP-MAS spectra of maltodextrin. Left: hydrated/gelated. Right: native powder (moisture level 12%).

The kinetic curves depicted in Fig. 3(A) and (B) show that the ageing kinetics of the inulin and maltodextrin gels differ. For the maltodextrin gel, directly after preparation no Gaussian contribution to the line shape can be observed. Under the conditions applied, the growth of the immobilized fraction in the maltodextrin gel stops after a few hours. This kinetics of solid phase formation correlates quite well with the results reported earlier on other maltodextrins obtained with the FID analysis method (Schierbaum et al., 1992). In the inulin gel, solidification occurs on a much shorter time scale than in the maltodextrin gel. For the 35% inulin gel a large fraction of the polymer is immobilized directly after preparation. As can be seen from Fig. 3 the increase of the Gaussian line shape component in the inulin gel $M_{za}(\Delta)$ spectrum is completed in less than 2 h. Lowering the inulin concentration to 30% results in less Gaussian line shape present directly after dissolution and in slowing down of the kinetics. For this gel, the Gaussian fraction of the $M_{za}(\Delta)$ lineshape equilibrates after 3 h, but at a lower value than for the 35% inulin gel. This indicates a lower degree of inulin solidification and gel firming at lower concentration.

The solid-like components observed in the inulin gels made at 60°C were considered to be due to incomplete dissolution, leaving some crystalline nuclei in suspension. These nuclei facilitate the crystallization process and contribute to the solid-like component detected in the spectra. Considering that inulin fully dissolves at temperatures in excess of approximately 82°C, we also examined a solution prepared at 85°C. Its $M_{za}(\Delta)$ spectrum showed the absence of the Gaussian line shape (solid-like) directly after preparation. During the first 60 min only the liquid-like component is detectable, after which the formation of a stable gel starts. The kinetics of the latter process is similar to that observed for the solution prepared at 60°C. The Gaussian fraction of the $M_{za}(\Delta)$ lineshape in both gels (same concentration) is the same after about 7 h. From our data it can be inferred that neither the kinetics of the solidification process, nor the final amount of solid-like component is influenced by the temperature at which the starting solution has been prepared.

Gel strength was also measured directly by rheological measurements. This showed that there was a good correlation between the θ values obtained from NMR experiments and G' values from rheological measurements. We can conclude that cross-relaxation NMR spectroscopy can be used as a rapid, simple and non-invasive method to probe gel firming.

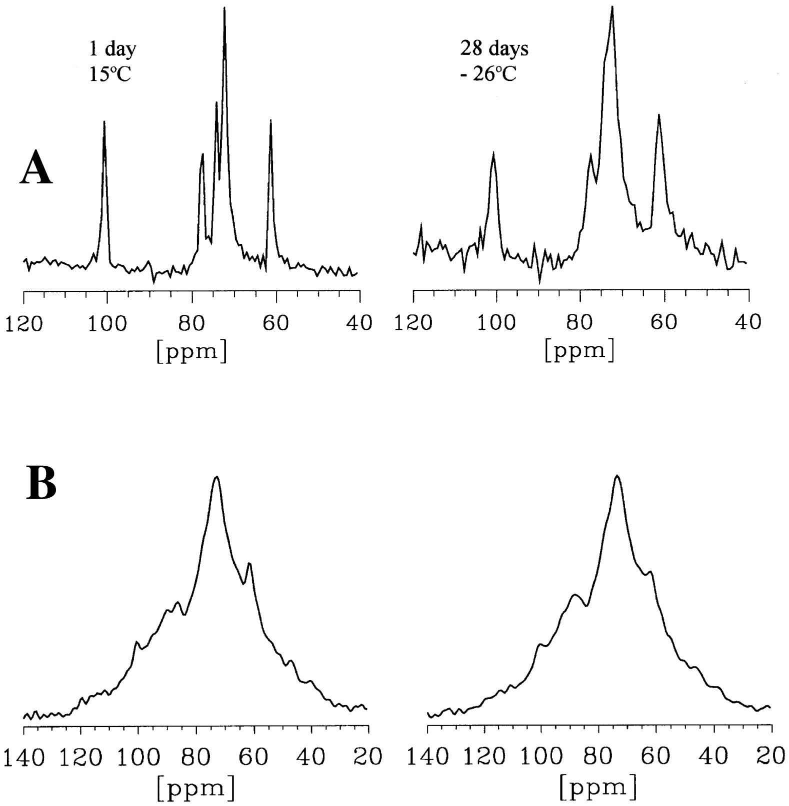

Fig. 5. (A) ^{13}C Bloch decay spectra of maltodextrin, obtained on static samples. Left: stored 1 day at 15°C (HT gel). Right: stored 28 days at −26°C (LT gel). (B) ^{13}C CP spectra of the same (static) maltodextrin samples.

3.3. One-dimensional ^{13}C solid-state NMR

Figs. 2 and 3 clearly show that cross-relaxation spectra of maltodextrin gels undergo their most dramatic change during the first 5 h. In order to probe the state of the gel after this initial period, ^{13}C NMR spectroscopy has been applied. Fig. 4 shows ^{13}C CP-MAS spectra of native maltodextrin powders (moisture level of 12%) and gelled maltodextrin (see Section 2). The line shapes in the spectra are similar to those reported earlier (Mora-Guitierrez & Baianu, 1991). These spectra show distinct spectral lines corresponding with various carbon positions in the glucose rings. Line shapes observed for the hydrated/gelated sample are much narrower than for dry samples. Also apparent is the absence of a resonance at the “amorphous” position of the C-4 carbon, indicating that the polysaccharide is in a crystalline form (Gidley, 1992). In earlier studies on hydrated starch, the narrowing of the ^{13}C resonances was exclusively ascribed to the increase in short-range order in the crystalline regions and the presence of fast molecular mobility was excluded. This is in line with results from X-ray diffraction studies (Veregin, Fyfe, Marchessault & Taylor, 1986).

The molecular mobility in maltodextrin gel was studied by recording static Bloch decay NMR spectra. These spectra are sensitive to motions on the time scale of 1 ns or shorter. Fig. 5(A) shows static Bloch decay ^{13}C NMR spectra revealing the presence of a liquid-like component. These highly mobile chains are in solution and do not contribute to the polymer network. The resolution is better for the HT gel than for the LT gel indicating that molecular mobility in the HT gel is higher. This is presumably due to less hindrance of the mobile chains as a result of a lower degree of association.

Mobility of the polymers on the time scale of kHz can be probed by recording CP spectra under static conditions. The line shapes obtained under these conditions are broadened by anisotropic interactions which render them sensitive to molecular motions in the kHz-regime (the size of the anisotropy). Fig. 5(B) shows static ^{13}C CP spectra of the HT and LT maltodextrin gels. Lines are broad and nearly structureless when compared with the CP-MAS spectra shown in Fig. 4. No change in the spectra is visible, revealing the absence of large amplitude motions with rates exceeding the width of the CP spectrum, i.e. above 20 kHz.

3.4. $T_{1\rho}$ (^{1}H) NMR relaxation measurements

Additional information on the local dynamics in the gels was obtained from rotating frame $T_{1\rho}$ (^{1}H) measurements. These relaxation parameters were obtained by monitoring

Table 1
$T_{1\rho}$ (^{1}H) relaxation rates (ms) and relative proportion of the Lorentzian component $(1 - \Phi)/\Phi$ in the ^{1}H WISE lineshapes obtained for maltodextrins gels

Preparation	$T_{1\rho}$ (^{1}H) dried	$T_{1\rho}$ (^{1}H) gel	$(1 - \Phi)/\Phi$
Native powder	5.5		
1 day at 15°C (HT)	3.95	20.2	0.038
28 days at 15°C	3.96	24.0	0.047
28 days at − 26°C (LT)	3.98	27.8	0.065

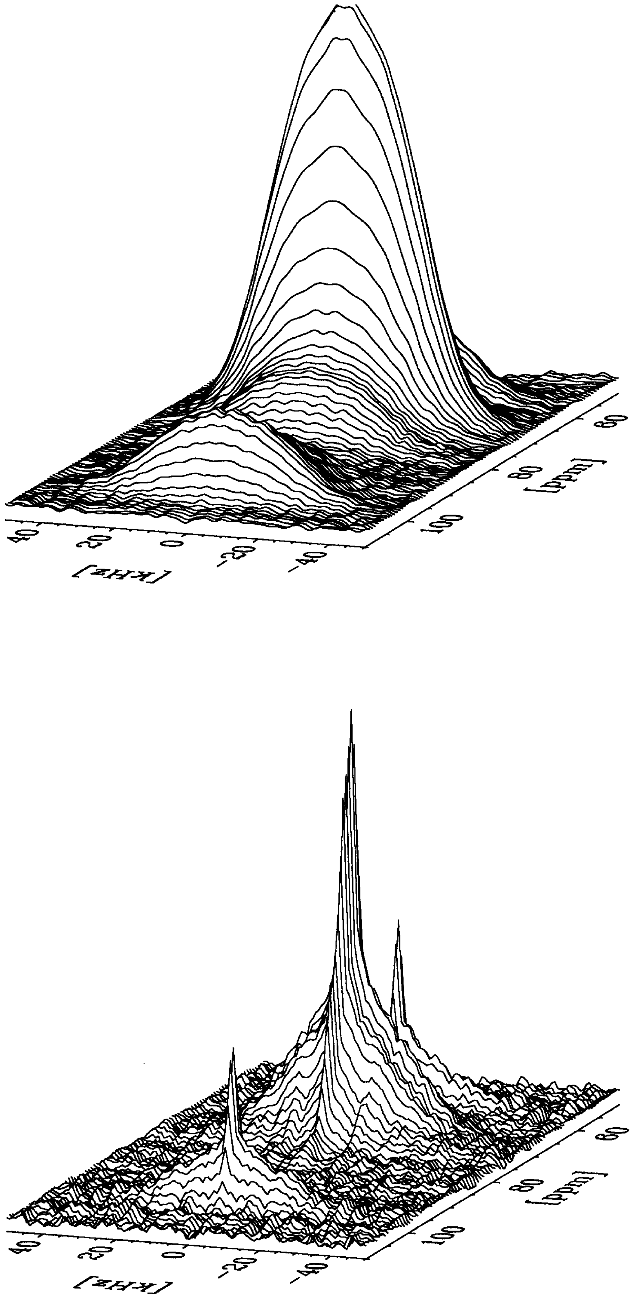

Fig. 6. WISE-NMR spectra of native maltodextrin powder (12% moisture) (upper plot) and hydrated maltodextrin (lower plot). For every carbon position the corresponding ^{1}H line is plotted.

the well resolved carbon signals in the ^{13}C CP-MAS spectra, as a function of the duration of the cross-polarization spin-lock field. Table 1 lists averaged values of the rotating-frame proton relaxation time $T_{1\rho}$ (^{1}H) as measured through several of the resolved ^{13}C NMR resonances in all samples studied. There is no difference in relaxation times of the respective ^{13}C NMR nuclei on the various positions of the glucose rings. This is due to the process of spin diffusion which averages magnetization at various positions of the glucose ring and yields one uniform value of $T_{1\rho}$ (^{1}H) for every sample listed in Table 1. There is a remarkable difference between $T_{1\rho}$ (^{1}H) in the gelled and native, dried samples (moisture level 12%). The $T_{1\rho}$ (^{1}H) values for the dried samples are smaller by almost one order of magnitude than in the gel state. $T_{1\rho}$ (^{1}H) values in the dry state for all gelled samples are the same. However, they differ from the values observed for native maltodextrin. This reveals changes at the macroscopic scale which are apparent after gelation.

For gels, $T_{1\rho}$ (^{1}H) values change as a function of preparation conditions. We note that $T_{1\rho}$ (^{1}H) values are measured indirectly by monitoring intensities of polysaccharide ^{13}C resonances as a function of the duration of the ^{1}H spin-lock field. During this period, the interaction of water molecules with the polysaccharide chain will prolong the $T_{1\rho}$ (^{1}H) values. From the values in Table 1 we can deduce that the gels stored for prolonged times at low temperature (LT gel) contain a higher amount of aggregated polymer chains/solid-like structures with an increased fixation of water.

3.5. Two-dimensional WISE-NMR

Interaction of water molecules with the polymer matrix can be demonstrated directly by means of 2D WISE spectroscopy (Ganapathy et al., 1994; Kulik et al., 1994; Schmidt-Rohr & Spiess, 1994). Fig. 6 shows 2D WISE spectra of dry (moisture level 12%) and gelated maltodextrin. For every distinct ^{13}C NMR resonance a proton line is obtained. The resolution along the ^{13}C axis is the same as that shown in Fig. 4. Pronounced differences are observed between the two physical states. In the gelated state a narrow component in all ^{1}H lines is visible. We note, that lines obtained for dry maltodextrin are broad and structureless. The half-width at half-maximum of the lines is about 50 kHz. This is typical of rigid solid components and indicates the absence of molecular motions in the tens of kHz regime. Similar results were reported for polysaccharide chains in maize starch (Kulik et al., 1994). More detailed information about gels is available by inspection of the ^{1}H widelines belonging to the various ^{13}C resonances (Fig. 7).

The ^{1}H NMR lines of maltodextrin gels exhibit a broad and a very narrow component which originate from non-exchangeable protons covalently attached to the immobile polysaccharide chains, and water-exchangeable protons of the polymer plus water in the vicinity of these chains (Ganapathy et al., 1994; Kulik et al., 1994). With respect

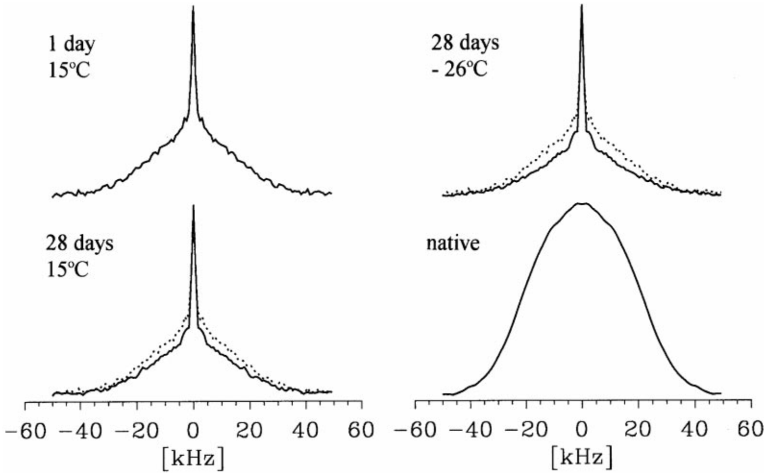

Fig. 7. Projection on the ^{1}H dimension of the WISE spectra for various preparation conditions. The dotted line is the line shape obtained from a gel stored for 1 day at 15°C (HT).

to the latter type of protons, we note that the WISE experiment cannot distinguish the rapid exchangeable hydroxyl groups from water in close proximity to the polymer chains.

No attempt was made to fit the ^{1}H WISE line shapes to theoretical models. Instead, the WISE ^{1}H line shapes were analyzed by simple deconvolution in Gaussian and Lorentzian line shapes (see Section 2). The relative proportion of the Lorentzian line shape, $(1 - \Phi)/\Phi$, can be considered as a measure for the interaction between water and the protons in the polysaccharide chains. Results of the analysis are collected in Table 1, and show that the values for $(1 - \Phi)/\Phi$ depend on the gel studied. The highest value of $(1 - \Phi)/\Phi$ is observed for the LT gel and the smallest one for the HT gel, indicating that the largest interaction between water and the rigid polymer matrix takes place in the LT gel. This is in accordance with the conclusion drawn from the $T_{1\rho}$ (^{1}H) results (vide supra).

For all datasets, the Gaussian (f_G) line shapes could be described with a (relaxation) time constant of 12 μs. This value is of the same order of magnitude as the value obtained for the solidified phase from the cross-relaxation experiment (17 μs). We note that although ^{1}H lines obtained with the cross-relaxation and WISE experiments have similar shapes, they may yield information about protons in different regions of the solid domains. In the cross-relaxation spectrum, the line shape is for a major part determined by the protons near the hydration interface, while in the WISE ^{1}H line shapes the dipolar couplings between all rigid protons are taken into account. The somewhat narrower Gaussian lineshape obtained from the cross-relaxation experiment may reflect a higher degree of mobility near the hydration interface.

4. Conclusions

^{1}H cross-relaxation NMR of model gels made from the carbohydrate-based fat replacers inulin and maltodextrin revealed that during the ageing process, the amount of immobilized polymer increases. The increase of the immobile fraction is explained by the formation of crystalline regions. The molecular mobility of the carbohydrate chains in these regions does not evolve during the ageing process. From the growth rate of the solid-like component in the gels different kinetics of ageing (crystallization) for inulin and maltodextrin were deduced. For the inulin gel it was observed that the fraction of immobilized material declines at lower starting concentration leading to a lower gel strength. Likewise, the final fraction of immobilized material in inulin gel after equilibration appeared to be independent of the preparation temperature. A longer time is required for firming of inulin gel when the starting polysaccharide material is totally dissolved, at temperatures in excess of 82°C. Likewise, investigation of structure formation in maltodextrin gels by solid-state NMR yielded information about mobility of polysaccharide chains and their interaction with water molecules. The molecular mobility of the polymer chains in solution was found to be higher in gels stored at higher temperatures. Lower molecular mobility of polysaccharide in gels stored at lower temperature was apparently due to the formation of a 3D polymer network accompanied by partial crystallization. Combination of cross-relaxation and solid-state NMR spectroscopy offers a convenient, non-destructive and quantitative way to characterize multiphase systems in terms of solid-like/liquid-like components.

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