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A pulsed ^{1}H NMR study of the hydration properties of extruded maize–sucrose mixtures

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The molecular mobility in maize and maize-sucrose extudates was studied as a function of the degree of hydration (up to 35% w/w dry basis) using proton spin-spin relaxation NMR. The extrusion of maize systems was found to enhance the molecular mobility of the constituents generating the rigid 'solid-like' and the mobile 'liquid-like' components of the NMR free induction decay signal.

As the moisture content was increased, the amplitude of the normalised NMR signal arising from the rigid component decreased dramatically for the samples containing sucrose, suggesting an increased mobility and thus a solution type behaviour of the sugar. This hypothesis was supported by the observation of shorter T_2 values for the liquid component of the signal recorded for the samples containing sugar. Sucrose was found to be miscible with the polysaccharide at moisture contents below 15%, but progressively dissolved into the additional water at higher moisture contents. This suggested the occurrence of phase separation over a short distance scale as the water content of the maize-sucrose system was modified. The results are discussed in terms of unequal water partitioning between the maize and the sugar components. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Since starch and starch-sugar extrudates are the basic constituents of many commercial products, it is not surprising that the effects of operational conditions and formulation on the resulting structural and functional properties of the extrudates have been extensively studied. Examples of such studies are those by Mercier *et al.* (1979) and Colonna *et al.* (1987).

More recently, the significance of the glass-rubber transition as an interpretive theme has been explored by Donald *et al.* (1993). Following the detailed study of the glass transition of biopolymers and the plasticizing effects of sugars by Kalichevsky *et al.* (1992) and the use of the Ten Brinke *et al.* (1983) and the Couchman-Karasz (Couchman *et al.*, 1978) equations to model the experimental behaviour of biopolymer-sugar systems, Fan *et al.* (1994, 1996) have exploited this information by initially modelling the expansion process and more recently rationalising the effect of sugars upon starch conversion within the extruder in addition to reducing the post-die expansion.

Somewhat surprisingly, comparatively limited information is available on the molecular interactions within such systems. Solid state NMR has been used by Farhat *et al.* (1996) to investigate the hydrocolloid-water interactions, and by Hansen *et al.* (1989) to study the sugar-starch interaction, while Lang *et al.* (1983) have used pulsed NMR to study the mobility of water in biopolymer and biopolymer-sugar systems. Farhat *et al.* (1996) have more recently exploited NMR techniques and X-ray diffraction to investigate the effects of various sugars on the kinetics of the starch retrogradation process.

It is now clear that whereas there is a large change in the mobility of the polymer at the glass transition temperature (Kalishevsky *et al.*, 1992), water molecules retain considerable mobility below the T_g of the hydrated system. In particular, Ablett *et al.* (1993) found no discontinuity in the self diffusion coefficient of water at T_g. The behaviour of intermediate sized molecules in such systems is less well characterized.

Pulsed NMR and molecular mobility

Pulsed NMR and particularly the spin-spin relaxation parameters provide a valuable tool for the investigation

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of molecular motions (Derbyshire, 1982). Several mechanisms could influence the loss of net magnetization in the xy plane M_{xy}. The rate of this relaxation mechanism, known as spin-spin relaxation is given by:

$$\frac{1}{T_2} = \frac{1}{T_1} + \gamma \Delta B$$

where T_1 is the spin-lattice or longitudinal (along the z-axis) relaxation time, γ the gyromagnetic ratio for the observed nuclear species, and ΔB the magnetic field dephasing contribution resulting from the presence of other resonant and non-resonant nuclei, chemical shift anisotropy, susceptibility effects and magnetic field inhomogeneity. The effect of the magnetic field inhomogeneity was first used by Stejskal *et al.* (1964) to study molecular diffusion. Rotational mobility information can be obtained from T_2 measurements (Oksanen *et al.*, 1993) as a result of the contribution of the other relaxation mechanisms. McBrierty *et al.* (1981) reviewed the relationship between the relaxation times and molecular correlation time.

The dephasing of a particular spin depends on the neighbouring dipoles. This relaxation mechanism is very efficient in solids where mobility is reduced and thus the static magnetic component created by neighbouring dipoles is large. In more mobile systems such as liquids, the static dipolar fields average out to very small values as a result of random molecular motion leading, to a less effective dephasing process and longer decay times (T_2) for the transverse magnetization (M_{xy}) (Martin *et al.*, 1980).

The objectives of the work described in this paper were therefore to investigate the effect of extrusion processing upon the molecular mobility of the polymer, and to determine the mobility of sucrose in the maize-sugar system as the system is plasticized by increasing the water content. The spin-spin NMR relaxation parameters were employed to study the molecular mobility of the various components in the system and determine whether sucrose was located in the rigid 'solid-like' or the mobile 'liquid-like' components over the range of moisture contents investigated.

MATERIAL AND METHODS

Materials and sample preparation

Maize grits were donated by Maizecor Foods Ltd. The specifications from the supplier indicated that these samples contained 8–9.5% protein, a maximum 1% of lipid, and that the starch was composed of approximately 25% amylose and 75% amylopectin. Commercial grade sucrose (British Sugar) was used in this work. The size of 90% of the particles ranged from 355 to 500 μm. Mixtures of maize grits and a known amount of sucrose (0%, 5% and 10% based on maize grits, % dry basis) were extruded at a water content of 18% (based on total solids fraction, % wet basis) and a temperature of 170°C using a Clextral BC21 co-rotating, intermeshing twin screw extruder as described by Fan *et al.* (1996a). A single 3.0 mm diameter circular die was used in the die plate. The feed rate was 11 kg/h.

After the expanded extrudates had been cooled, they and the raw maize grits were ground to fine powders using a laboratory mill with a 0.5 mm sieve. The powders were dried in a vacuum oven at 70°C for 15 hours and then hydrated isopiestically (Nyquist, 1983) over saturated salt solutions for 1 week at ambient temperature (25±2°C). This gave a range of moisture contents between 0 and 35 g of water per 100 g of dry solid.

NMR measurements

Proton relaxation NMR experiments were performed under standard conditions using a Bruker bench top Minispec PC120 (Bruker Spectrospin Ltd.) operating at a resonance frequency of 20 MHz, a temperature of 40±0.1°C and equipped with a phase-sensitive detector. The samples were sealed in 8 mm diameter NMR tubes. Typically 24 scans were accumulated with a recycle delay of 1 to 2 seconds.

The spin-spin relaxation parameters were obtained directly from the free induction decay (FID) recorded after the 90° excitation rf pulse. The dead time between the rf pulse excitation and the data acquisition was estimated to be 10 μs. Results were recorded along the x (M_x) and y (M_y) phases and the magnetization in the xy (M_{xy}) plane was obtained by combining M_x and M_y.

The spectrometer was equipped with a relatively slow digitizer (minimum dwell time of 30 μs) and thus provided little information concerning the fast decaying component ($T_2 < 40$ μs) of the FID. This was compensated by using an interleaved-FID pulse programme developed specifically for this spectrometer. The FIDs of 10 consecutive experiments with data points recorded at complementary times were merged enabling a 'virtual' dwell time of 2 μs for the period between 10 and 20 μs, 4 μs between 20 and 40 μs, 10 μs for times up to 240 μs and finally a dwell time of 30 μs for the remaining data points.

A non-linear fitting routine based on the minimisation of the least squared deviations was applied to the resulting decay which was best described using 2 gaussian components: a 'solid' component with decay times (T_2 solid) of a few tens of μs and a 'liquid' component with decay times (T_2 liquid) of a few hundreds of μs. These two parts of the FID were distinct and a minimum of one order of magnitude was observed between the relaxation times of the long and short decaying components.

As described earlier, the mobility of the observed ^1H containing molecular species is the only criterion governing their assignment to the solid or the liquid component of the NMR signal. The term 'solid' component refers to the molecules with limited mobility such as the polymer's C-H protons, while the liquid component refers to the more mobile protons such as the water ^1H and mobilised sugar molecules. Exchange of ^1H mainly from the hydroxyl groups introduces an additional complication which can cause exchangeable sugar and polymer protons to contribute to the 'liquid' component of the FID signal.

Other measurements

Wide angle x-ray scattering (WAXS) spectra of the fine powders were recorded using a Philips PW 1730 diffractometer. The x-ray generator was equipped with a copper source operating at 40 kV and 50 mA and generated radiation of wavelength 1.54 Å (CuK_α). X-ray diffractograms over the angular range 2θ between 4 and 38° and a spectral resolution of 0.05° were recorded as a function of sample composition (water and sucrose contents) at room temperature.

The sorption isotherms were defined at 26±2°C; the water contents were determined gravimetrically and the water activities were measured using a Decagon CX-1 Aw-meter.

RESULTS AND DISCUSSION

X-ray diffraction

The x-ray diffractograms were recorded on the native, extruded and extruded with 10% sucrose samples with different water contents in order to assess the crystalline order of the starch and of the sugar (Fig. 1). The native starch lost its A-type crystalline structure on extrusion. The x-ray pattern developed was characteristic of an amylose/lipid complex (Mercier *et al.*, 1979). Fan *et al.* (1996b) have already presented a detailed study of the effects of water and sugar contents on the form of this complex.

In general, the starch crystalline order was very small in the extrudates. The crystallinity indices were calculated using the method described by Hermans *et al.* (1948) based on the relative area under the characteristic sharp peaks. They were less than 2 to 4% in the extruded samples compared to 15–25% in the native material as the water content was increased from 5 to 25% (w/w dry basis). A notable feature was that no sharp peaks characteristic of crystalline sugars were observed in any of the x-ray diffractograms of the extruded maize grits — sucrose samples, implying the absence of crystalline sucrose over the entire range of moisture contents investigated.

These results are in agreement with those obtained by Fan *et al.* (1996b) on the same systems where they reported total starch conversion based on differential scanning calorimetry results at the levels of sucrose used here.

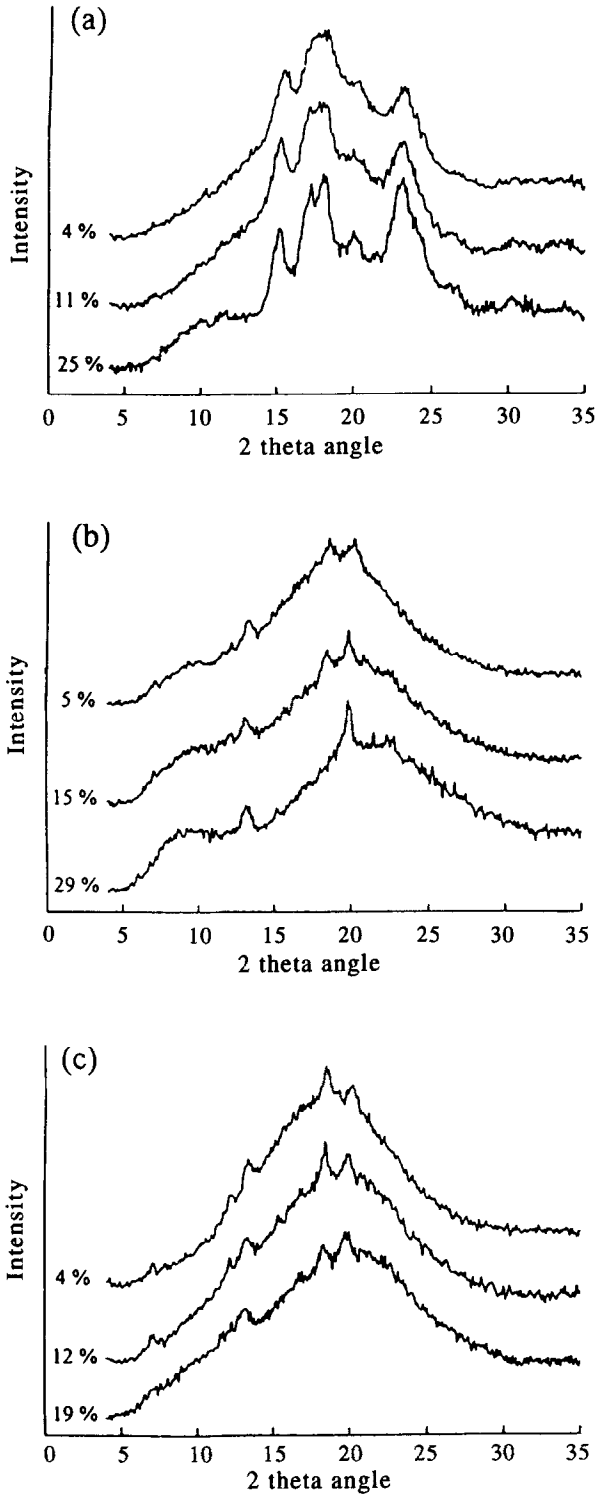

Fig. 1. X-ray diffractograms obtained for samples of maize grits at different water contents (w/w dry basis). (a) Native maize grits (4%, 11% and 25% water w/w d.s.b) (b) Extruded maize grits (5%, 15% and 29% water w/w d.s.b) (c) Maize grits extruded with 10% sucrose (4%, 12% and 19% water w/w d.s.b).

Time domain NMR

Effects of extrusion process on the nmr properties

All samples displayed a decay time (T_2) for the 'solid' component that increased with increasing moisture content which was consistent with a greater polymer segmental mobility induced by plasticization by water (Fig. 2). At low water levels, less than 16%, there was little difference between extruded and non-extruded samples but at higher water levels, the solid T_2 results showed a higher mobility for the various polymers (amylopectin, amylose and proteins) in the extruded material. These observations are consistent with the following interpretation. Intact starch granules, which are present only in the native samples, can only absorb a certain volume of water, which will serve as a plasticizer. At water contents below this limit, proton mobility is similar in gelatinized and non gelatinized samples. However, at higher water contents, the extruded gelatinized samples provide the water with a greater access to the starch polymers and permit a more effective plasticization.

This same pattern was observed for the 'liquid' T_2 where the values measured on the extruded samples were greater than those of the native samples. At higher water contents (>20%) the rate of proton exchange between water and the starch hydroxyl groups became important on the time scales of the NMR relaxation measurement. The increasingly effective exchange is demonstrated by a decrease in the recorded 'liquid' T_2. Under fast exchange conditions, the observed relaxation rate is the mean of the rate related to free water and to the exchangeable protons, inevitably dominated by the latter. An increase in the observed relaxation rate ($1/T_2$) is evidence of an increasingly effective exchange process.

Although extrusion cooking had an effect on the relaxation times of the rigid and the mobile components of the FID, no significant differences in the relative contribution of the mobile and rigid components to the total NMR signal were found (Fig. 3). A linear relationship between the NMR liquid/solid ratio and the water content was found. However, the proton densities of the maize and the water contents calculated as described in the next paragraph, predicted the solid line presented on the plot with a zero intercept and a slope of 1.794. Although the slope for the values obtained for water contents below 25% was as predicted by the ratio of the proton densities of water and the maize-sucrose mixture, the intercept was negative, leading to a value of approximately 2% water for a liquid/solid ratio of 0. These observations indicated that the calculation of the maize proton density described in the next section was a good approximation and that probably the first 2–3% of added water were so tightly bound to the solid matrix that the water protons contributed to the signal arising from the rigid-lattice.

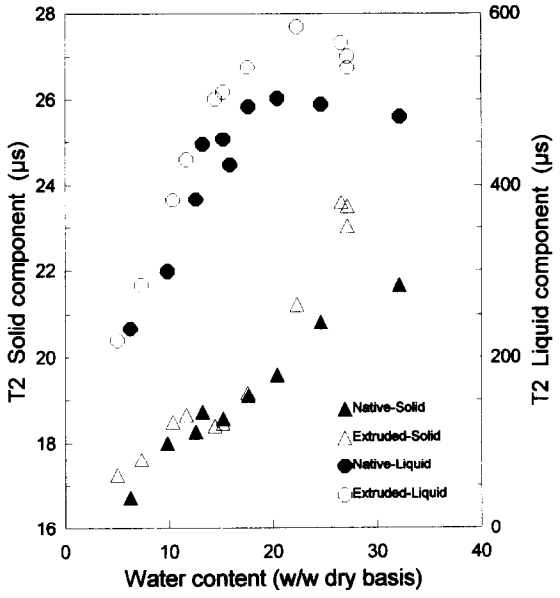

Fig. 2. The spin-spin relaxation times (T_2) of the solid and the liquid components of the NMR free induction decay. Results obtained on native and extruded maize grits at different degrees of hydration are compared.

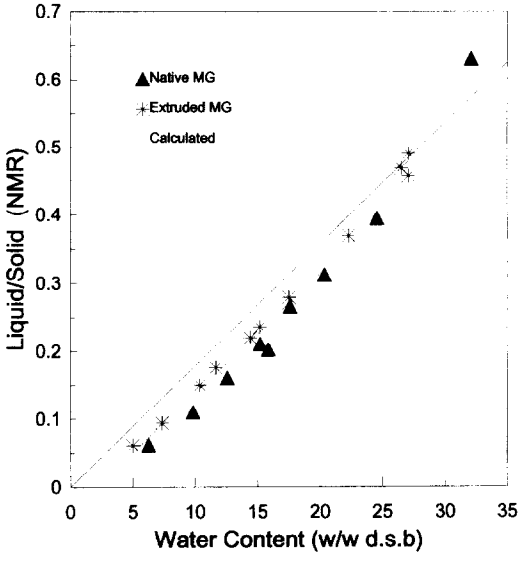

Fig. 3. The ratio of the NMR signal emanating from the 'liquid-like' NMR component relative to the 'solid-like' component as a function of the ratio of the water content as defined by oven drying.

Starch-sugar systems

The ratio of the liquid relative to the solid component of the FID signal measured on the samples containing sucrose became progressively larger with increasing water content compared to the values determined for the maize sample not containing sucrose (Fig. 4). The NMR signal amplitudes should, however, be described with respect to the proton densities of the various species in the system (proton density = number of protons per mass unit). Let S_{MG}, S_W and S_S be the contribution to the total NMR signal, S, resulting from

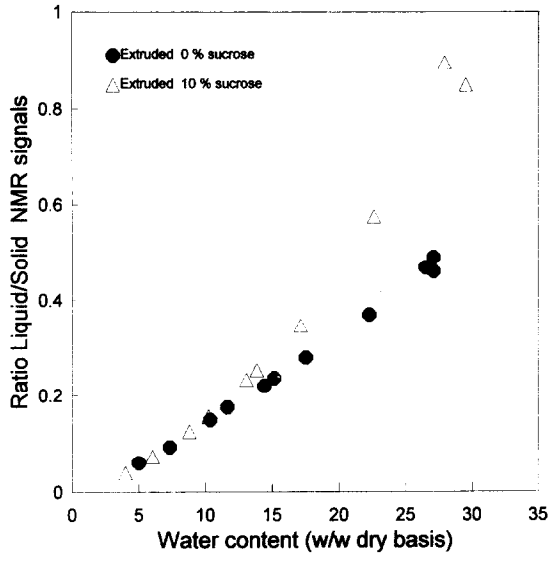

Fig. 4. The ratio of the liquid to solid NMR signals as a function of the water content for 2 sucrose concentrations (0% and 10%).

the biopolymers of the maize grits, the water and the sucrose respectively, and w_{MG} , w_W and w_S be the weight fraction of each of these species in the mixture. If d_{MG}, d_W and d_S denote the proton densities of the various components, the proton densities of water and sucrose are $d_W = 2/18$, $d_S = 22/342$ respectively. Due to the complex composition of the maize grits, d_{MG} was calculated assuming an approximate composition of 90% polysaccharides and 10% proteins. The proton density of the maize grits was calculated as the weighted proton density of these two components. The value used was $d_P = 0.0622$ (the proton density of starch being $d_{st} = 10/162$ ie 0.0617 and the proton density of protein was calculated assuming an equal composition of the 20 most common amino acids $d_P = 0.0665$). The expected contributions to the total FID signal, S, by the three constituents are:

$S_{MG} = k.w_{MG}.d_{MG}$ from maize grits
$S_S = k.w_S.d_S$ from sucrose
and $S_W = k.w_W.d_W$ from water; k being a constant factor.

Analysis of the resulting signal (A_{tot}) leads to the isolation of two constituent gaussian processes, each with an associated amplitude A_{sol} and A_{liq} representing the solid and liquid components respectively, which can be expressed as follows:

The solid component amplitude $A_{sol} = k(w_{MG}.d_{MG} + w_S.d_S)$ resulting from maize grits and sucrose.
The liquid component amplitude $A_{liq} = k.w_W.d_W$ resulting from water.
The total signal amplitude $A_{tot} = k(w_{MG}.d_{MG} + w_S.d_S + w_W.d_W)$

For purposes of description, it is often convenient to normalise all signals to an expected 'solid' signal defined as unity. The solid amplitude fraction of the total can then be described by:

$$A = \frac{A_{sol}}{A_{sol} + A_{liq}} \left(1 + \frac{w_W.d_W}{w_{MG}.d_{MG} + w_S.d_S}\right)$$

After this normalization, the solid amplitude would be constant and equal to 1 when plotted against the water content (Fig. 5). However, the values for the 0% sugar sample showed a small offset relative to 1. This is not unusual. In simple starch/water systems a small water fraction is apparently incorporated into the starch matrix and contributes to the solid signal. However, there is a second explanation, namely that the assumption concerning d_{MG} was incorrect as the protein composition was unknown and other biomolecules (lipids) which were not accounted for, were present in the system. However, this second hypothesis was discarded on the basis to the results in Fig. 3 which showed that the experimental (1.794) and theoretical ($d_W/d_{MG} = 1.786$) gradients were very similar.

The plot of the normalized solid amplitude versus water content clearly displayed the solvation process of sucrose and its subsequent participation in the aqueous phase signal. This suggestion is supported by the shorter T_2 values recorded for the liquid component at water contents above 10%. T_2 values are thought to be shortened by the increase of the viscosity of the aqueous phase through the presence of sucrose (Fig. 6).

The effect of sucrose content is shown in Figs 7, 8 and 9. The higher the sucrose content, the larger the changes of the amplitude of the solid component as the samples were hydrated (Fig. 8). At the higher water contents the solid amplitude was decreased by approximately 5% for the sample containing 5% sucrose and 10% for the sample containing 10% sucrose relative to the control

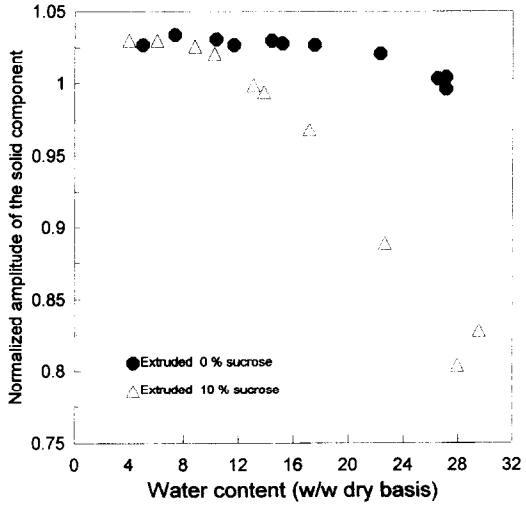

Fig. 5. The normalised amplitude of the rigid component of the FID plotted versus water content for 0% and 10% sucrose maize grits extrudates.

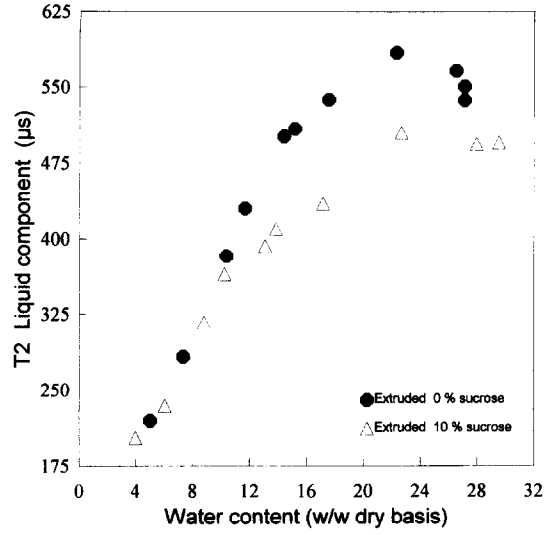

Fig. 6. The spin-spin relaxation time of the liquid component of the NMR free induction decay of extruded maize grits containing 0% and 10% sucrose as a function of the water content.

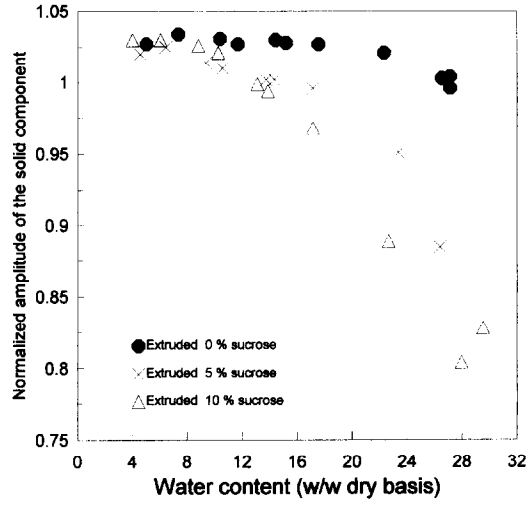

Fig. 8. Effect of sucrose content: the normalised amplitude of the solid FID component plotted versus water content for 0%, 5% and 10% sucrose in maize extrudates. The offset between the 3 lines is of the order of the difference in sucrose content (5%) between the 3 samples.

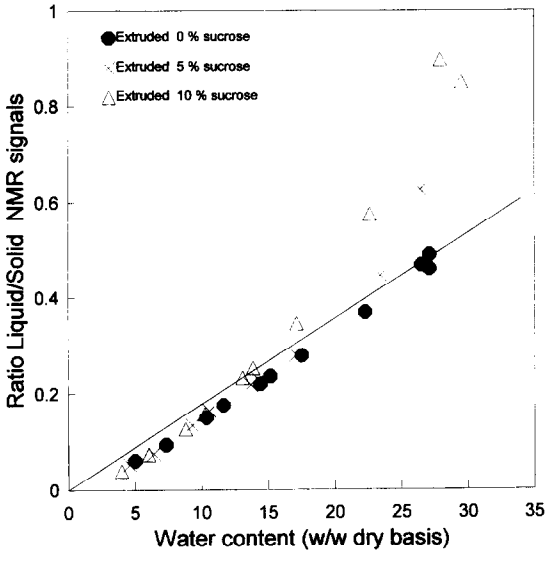

Fig. 7. Effect of sucrose content: the ratio of the liquid to solid NMR signals as a function of the water content for 0%, 5% and 10% sucrose in maize grit extrudates.

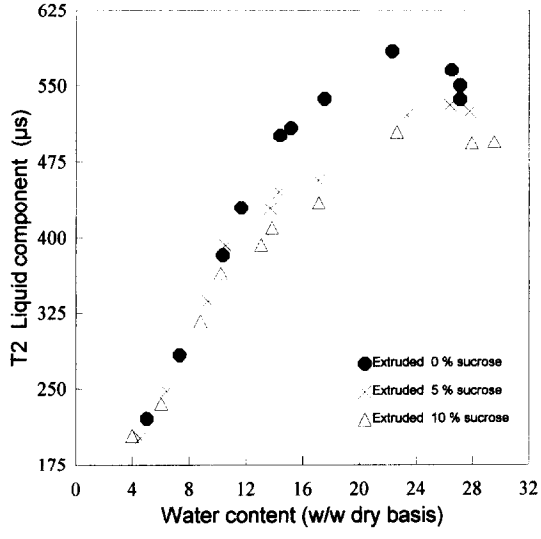

Fig. 9. Effect of sucrose content: the T_2 of the liquid FID component of extruded maize grits containing 0%, 5% and 10% sucrose plotted against water content.

(0% sugar). This suggests that the entire sucrose content was dissolved in the aqueous phase at approximately a moisture content of 25%. Above this water content, the increase in the relative amplitude of the NMR signal is greater than the total amount of sucrose present in the system. This points to a contribution from the maize grit protons to the signal resulting from the liquid component as the rate of proton exchange between the polymer and the water increases, and the mobility of the biopolymers increases due to the plasticizing effect of water. The decrease in the relaxation times of the liquid component was proportional to the sucrose content (Fig. 9), a consequence of the increase in the viscosity of the liquid phase with increasing sucrose content.

These observations suggest that the roles of water and sugar in plasticizing biopolymers may be more complex than is assumed in the derivation of the Ten Brinke (Ten Brinke *et al.*, 1983) and the Couchman-Karasz (Couchman *et al.*, 1978) equations. To determine whether this is so, we can calculate, using these equations, the water content at which a T_g of 40° (the temperature at which the NMR measurements were performed) should be observed and compare these values with those where a contribution of the protons of the 'solid' component to the 'liquid' component of the NMR signal is observed.

Such calculations show that the T_g is equal to 40°C at approximately 22% (w/w d.s.b) for the system contain-

ing no sucrose and 21 and 19% for the 5 and 10% sucrose systems respectively. The contribution of the polymer protons to the liquid NMR signal is observed at water contents above 24% (w/w d.s.b). The appearance of sucrose in the liquid NMR signal is observed at approximately 17 and 11% for the samples containing 5 and 10% sucrose respectively. A clear correlation between these water contents and the glass transition parameters suggests that the generation of a concentrated sucrose solution promotes the plasticization of the polymer component. We suggest, however, that one additional factor should be taken into account when considering ternary systems, namely the differential partitioning of water between the different components.

Despite the reasonably close correlation found by Kalishevsky *et al.*, 1993 between the experimental T_g values and those calculated using the Ten Brinke *et al.* (1983) and the Couchman–Karasz (Couchman *et al.*, 1978) equations, it is clear that in sugar containing systems there is a small but systematic departure from the calculated values. The measured values were smaller at low water contents and greater at high water contents. Since the T_g will be greatly influenced by the amount of the plasticizer within the polymer domains, it seems possible that these deviations could be explained by a partitioning of water between the various components such that water is preferentially associated with the polymer at low water contents and with the sugar at higher water contents. The unequal partitioning of water hypothesis is in agreement with the work of Hartley *et al.* (1995) describing the hydration of biopolymer mixtures.

This differential water partitioning concept could imply that the effective T_g values of the systems investigated in this work are lower than the calculated values and therefore the water contents at which the T_g of these samples is equal to 40°C are lower than predicted by the Ten Brinke equation. This would consolidate the hypothesis of a direct relationship between the glassy/rubbery state of the polymer and the mobility of the sugar.

The water vapour sorption isotherms of amorphous sucrose (25°C) (Iglesias *et al.*, 1982) and extruded maize measured at 25°C are shown in Fig. 10. For reasons of clarity, only the GAB (Guggenheim–Anderson–DeBoer) fit of the measured water adsorption values on maize grit samples is represented as this model was found to give a satisfactory description of water sorption isotherms (Van den Berg, 1985).

For water activities higher than 0.45, the affinity of water for sucrose is greater than that for maize. The value of $aw = 0.45$ corresponds to water content of 10% approximately. This is in good agreement with the value of water content where the dissolution of sucrose was observed by NMR (15%).

These results are in agreement with the FT-IR and DSC studies of Pautrat *et al.* (1995) in which they

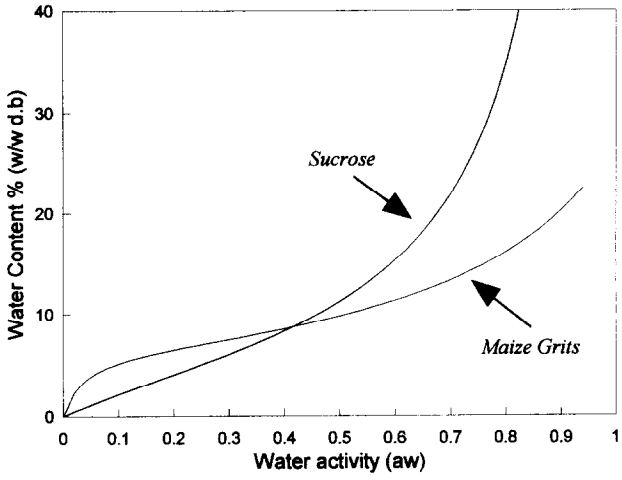

Fig. 10. Water vapour sorption isotherms (25°C) of amorphous sucrose (Iglesias *et al.*, 1982) and maize extrudate.

describe the changes they observed in terms of the establishment of hydrogen bonds which they equated with dissolution. Using this definition, it appears that sucrose is incorporated into the solid ie polymer phase at moisture contents below 15%, but that at higher water contents the dissolution of the sucrose in the aqueous phase occurs. Furthermore, the absence of any evidence of sucrose crystallisation in the X-ray scattering spectra of the samples recorded at different water contents supports the view that the sucrose is fully miscible with the polymer phase at low water contents and in the aqueous phase at high water contents over the whole range of sugar concentrations investigated in this work.

Hydration of binary systems

Based on the results described above, in addition to unpublished FTIR work on the hydration of protein-sugar systems, a model of the hydration of biopolymer-sugar systems may be suggested (Fig. 11).

The drying of the homogeneous maize-sucrose-water melt containing approximately 22% water (w/w d.s.b) was achieved by evaporation of the water when the product emerged from the extruder die at a temperature just under 170°C and by subsequent oven drying (Fig. 11a & b). As the sample is rehydrated (Fig. 11c), the first water molecules (water contents < 10–15%) preferentially bind to the biopolymer mixtures (starch and proteins). Further hydration (a second stage) is accompanied by the sugar binding the majority of the added water. The implication of this second stage is that a 'solution-type' behaviour is demonstrated by the NMR properties of the sugar molecules which now contribute to the slow decaying mobile component of the FID. The relaxation and the glass-rubber transition of the biopolymers would take place during this hydration process.

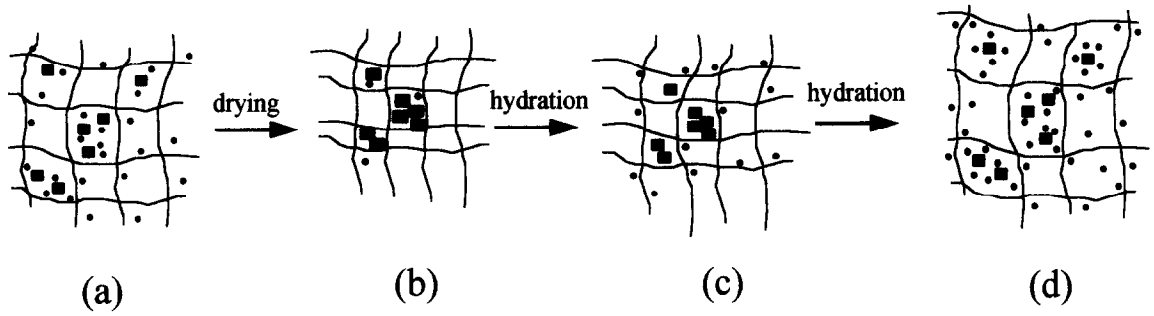

Fig. 11. Schematic representation of the effect of the drying-hydration cycle on the different components of a biopolymer-sugar system (the biopolymer network is represented by the solid lines, the sugar molecules by the shaded squares and the water molecules by the dots): (a) The maize-sucrose-water melt inside the extruded barrel at approximately 22% water (w/w d.s.b) and 170°C. (b) The same system after the majority of water was eliminated by evaporation at the exit of the extruder and subsequently by oven drying. (c) The first steps of hydration (up to water contents of 10–15%). The biopolymers are being preferentially hydrated. (d) Further hydration where the hydration of sucrose was achieved by the additional water molecules.

CONCLUSION

Processing has a major effect on the molecular mobility of the various components in food systems.

The results suggest an increase in sugar mobility at water contents above 10–15% when starch-sugar mixtures are progressively hydrated leading to a sugar-water aqueous phase. This solvation process can be probed by time domain NMR since it affects both the signal amplitude and the relaxation rates of the solid and liquid components. The assumption that the starch/sugar/water ratios are constant over the entire moisture content range is therefore not valid as the partitioning of sugar between the solid and liquid phases changes with increasing hydration. This last statement does not exclude the possibility of interactions between the sugar molecules and the biopolymer. Indeed, the absence of a crystalline sucrose phase, especially at low and intermediate water contents, points to such interactions.

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REFERENCES

Ablett, S., Darke, A.H., Izzard, M.J. & Lillford, P.J. (1993). Studies of the glass transition in malto-oligomers, *The Glassy State in Foods*, edited by Blanshard, J. M. V. and Lillford, P. J., Nottingham University Press, 189–206.

Colonna, P., Buleon, A. & Mercier, C. (1987). Physically modified starches, *Starch: Properties and Potential*, edited by Galliard, T., John Wiley and Sons, New York, 79.

Couchman, P.R. & Karasz, F.E. (1978). A classical thermodynamic discussion of the effect of composition on glass transition temperatures. *Macromolecules*, **11**, 117–119.

Derbyshire, W. (1982). The dynamics of water in heterogeneous systems with emphasis on subzero temperatures, *Water: A Comprehensive Treatise*, edited by Franks, F., Plenum Press, New York, **7**, 339–430.

Donald, A.M., Warburton, S.C. & Smith, A.C. (1993). Physical changes consequent on the extrusion of starch, *The Glassy State in Foods*, edited by Blanshard, J. M. V. and Lillford, P. J., Nottingham University Press, 375–393.

Fan, J., Mitchell, J.R. & Blanshard, J.M.V. (1994). A computer simulation of the dynamics of bubble growth and shrinkage during extrudate expansion. *J. Food Engineering*, **24**, 337–356.

Fan, J., Mitchell, J.R. & Blanshard, J.M.V. (1996). The effect of sugars on the extrusion of maize grits: I. The role of the glass transition in determining product density and shape. *Int. J. Food Technology*, **31**, 55–65.

Fan, J., Mitchell, J.R. & Blanshard, J.M.V. (1996). The effect of sugars on the extrusion of maize grits: II. Starch conversion, *Int. J. Food Technology*, **31**, 67–76.

Farhat, I.A., Moreau, P., Mitchell, J.R., Derbyshire, W. & Blanshard, J.M.V. (1996). Spectroscopic studies on hydrocolloid water interactions, *Proceedings of the Eighth Conference on Gums and Stabilizers for the Food Industry*. Wrexham-UK, 1995, in press.

Farhat, I.A., Blanshard, J.M.V., Melvin, J.L. & Mitchell, J.R. (1996). The impact of amylopectin-sugar interactions on molecular motion and order, Paper presented at the *Starch: Structure and Function international conference*. Cambridge-UK, 1996, in press.

Hansen, L.M., Setser, C.S. & Paukstelis, J.V. (1989). Investigations of sugar-starch interactions using C-13 nuclear magnetic resonance: 1. Sucrose. *Cereal Chemistry*, **66**(5), 411–415.

Hartley, L., Chevance, F., Hill, S.E., Mitchell, J.R. & Blanshard, J.M.V. (1995). Partitioning of water in binary biopolymer mixtures at low water content. *Carbohydrate Polymers*, **28**(2), 83–89.

Hermans, P.H. & Weidinger, A. (1948). *Journal of Applied Physics*, **19**, 491.

Hills, B.P., Takacs, S.F. & Belton, P.S. (1990). A new interpretation of proton NMR relaxation time measurements of water in food. *Food Chemistry*, **37**, 95–111.

Iglesias, H.A. & Chirife, J. (1982). *Handbook of food isotherms*, Academic Press.

Kalichevsky, M.T., Jaroszkiewicz, E.M., Ablett, S., Blanshard, J.M.V. & Lillford, P.J. (1992). The glass transition of amylopectin measured by DSC. DMTA and NMR. *Carbohydrate Polymers*, **18**, 77–88.

Kalichevsky, M.T., Jaroszkiewicz, E.M. & Blanshard, J.M.V. (1992). Glass-transition of gluten: 1. Gluten and gluten sugar mixtures. *Int. J. Biol. Macromol.*, **14**(5), 257–266.

Kalichevsky, M.T., Jaroszkiewicz, E.M. & Blanshard, J.M.V. (1993). A study of the glass-transition of amylopectin sugar mixtures. *Polymer*, **34**(2), 346–358.

Kalichevsky, M.T. & Blanshard, J.M.V. (1993). The effect of fructose and water on the glass-transition of amylopectin. *Carbohydrate Polymers*, **20**, 107–113.

Lang, K.W. & Steinberg, M.P. (1983). Characterization of polymer and solute bound water by pulsed NMR. *Journal of Food Science*, **48**, 517–520.

Martin, M.L., Delpuech, J.J. & Martin, G.J. (1980). *Practical NMR Spectroscopy* Heyden & Son Ltd., 14–20.

McBrierty, V.J.& Douglass, D.C. (1981). Recent advances in the NMR of solid polymers. *Journal of Polymer Science: Macromolecular Reviews*, **16**, 295–366.

Mercier, C., Charbonnière, R., Gallant, D. & Guilbot, A. (1979). Structural modification of various starches by extrusion cooking with a twin-screw French extruder, *Polysaccharides in Foods*, edited by Blanshard J. M.V and Mitchell J.R, Butterworths, London, **10**, 153–170.

Nyquist, H. (1983). Saturated solutions for maintaining specified relative humidities. *Int. J. Pharm. Tech. & Proc.*, **42**, 47–48.

Oksanen, C.A. & Zografi, G. (1993). Molecular mobility in mixtures of absorbed water and solid poly(vinylpyrrolidone). *Pharmaceutical Research*, **10**(6), 791–799.

Pautrat, C., Bressan, C. & Mathlouthi, M. (1995), Physico-chemical study of the effect of some polysaccharides on the sucrose crystallization conditions, in press.

Stejskal, E.O. & Tanner, J.E. (1964). Spin diffusion measurements spin echo in presence of a time-dependent field gradient. *Journal of Chemical Physics*, **421**, 288–292.

Ten Brinke, G., Karasz, F.E. & Ellis, T.S. (1983). Depression of the glass transition temperatures of polymers networks by diluents. *Macromolecules*, **16**, 244–249.

Van den Berg, C. (1985). Development of B.E.T-like models for sorption of water on foods, theory and relevance, *Properties of water in food*, edited by Simatos, D. and Multon, J.L, 119–131.