Mobility Characterization of Waxy Corn Starch Using Wide-Line ^{1}H Nuclear Magnetic Resonance

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The molecular mobility of waxy corn starch was studied by using wide-line ^{1}H nuclear magnetic resonance (NMR) spectroscopy. A suite of NMR techniques was used to measure relaxation times (i.e., T_2^*, T_2, and T_1) and to characterize water and solid (starch) mobility of waxy corn starch. It was observed that the spectrum of each sample includes a complex broad proton component upon which is superimposed a narrow proton component over water activity (a_w) ranges from 0.33 to 0.97 (i.e., 10.−25.6% water content) at 25 °C. Line shape analysis and relaxation times of both broad and narrow components show that T_2^* and T_2 values decrease (i.e., decreasing mobility) with increasing solid concentration and show a "break point" in a concentration range between 19.8 and 21.9% water content. The T_1 shows a "T_1 minimum" in the same concentration range. Starch samples change from the glassy to viscous rubbery state in this same concentration range. This demonstrates that wide-line ^{1}H NMR relaxation times (i.e., T_2^*, T_2, and T_1) may be useful as indicators of glass transition for starch samples in the solid state. The results demonstrate that wide-line ^{1}H NMR spectroscopy is able to separate modes and quantitate the magnitude of molecular mobility in complex systems.

INTRODUCTION

Proton (^{1}H) nuclear magnetic resonance (NMR) spectroscopy is a potentially powerful tool for studying the dynamic aspects of the interactions of water with biopolymers. In dilute biopolymer solutions and gels, the majority of water molecules are expected to move freely (i.e., mobile water) and undergo rapid motion. ^{1}H NMR spectrum is therefore dominated by the bulk water signal, and the relaxation characteristics are determined mainly by water proton exchange with the biopolymer's proton (Belton et al., 1993; Belton, 1997). Little information can be obtained about the water dynamics from ^{1}H NMR relaxation measurements in the high-moisture samples. However, for biopolymer systems containing small amounts of water, the bulk water signal is either absent or greatly reduced and proton exchange is expected to be much slower (Hills et al., 1991; Tanner et al., 1991). Therefore, it is possible to use ^{1}H NMR to probe the water dynamics in low-moisture samples (water content < 35%). The slowing of water motion at low-moisture samples has been reported to be associated with "bound" water (i.e., immobile water) arising from hydrogen bonding (Leung et al., 1983; d'Avignon et al., 1988; Chen et al., 1997; Hills and Manning, 1998). Water mobility in food systems was often characterized by its NMR spin−spin relaxation time. A two-state fast exchange model has been the major model used to interpret NMR data (Finney et al., 1982). However, the two-state model with fast exchange holds only for dilute solutions (>60%

water content); at lower water concentrations, deviations from linearity have been observed (Richardson et al., 1986, 1987a,b).

The interactions of water with starch have important consequences in a number of areas, such as in affecting the extent of crystallinity and the dynamics of the starch chains. Water is known to affect the glass transition temperature (T_g) and hence will affect the rate of recrystallization of amorphous starch and the material properties (Zeleznak and Hoseney, 1987; Roos and Karel, 1991). Moreover, the migration of water has been implicated in the staling of bread and influences the spoilage of starch through microbiological activity (Kim-Shin et al., 1991; Chen et al., 1997; Hills et al., 1997; Kou et al., 1999).

Molecular mobility in food systems (i.e., water mobility, solids mobility, and glass transition temperature of food system) has a pronounced influence on many important aspects of food stability and safety (Chinachoti and Schmidt, 1991; Slade and Levine, 1991; Chen et al., 1997; Li et al., 1996, 1998; Kou et al., 1999). Water and solids mobility in food systems is often related to such phenomena as diffusion, viscosity, and glass transition. In recent years, evidence suggests that water and solids mobility is related to many important diffusion-limited properties of foods (Fennema, 1996). When a food is cooled and/or reduced in water content so that all or part of it is converted to a glassy state, molecular mobility is greatly reduced and the food becomes more stable. It has been recognized that the mobility of food systems as measured by T_g can determine the processibility, product properties, quality, stability, and safety of the food system.

NMR is a powerful spectroscopic technique that allows the water and food solids (e.g., carbohydrates and

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proteins) mobility to be studied independently (Belton et al., 1993; Gil et al., 1996). Therefore, NMR spectroscopy has been used as a complementary technique to differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) with the aim of obtaining a better understanding of the water and food solids mobility in food systems (Schmidt and Lai, 1991; Kalichevsky et al., 1992; Wu et al., 1992; Ablett et al., 1993; Li et al., 1996, 1998; Kou et al., 1999). Actually, many attempts have been made to use water mobility (as monitored by NMR water relaxation time) as a measure of water availability and to use the glass transition temperature (T_g) as an indicator of the overall mobility of food systems (Schmidt and Lai, 1991; Slade and Levine, 1991; Belton et al., 1993; Gil et al., 1996; Kou et al., 1999). However, very little work has been done on the relationship between the water and solids mobility and the glass transition temperature in food systems and their relationship to food stability.

Although there have been a number of NMR studies of hydrated starch, information regarding water mobility and solids mobility in the solid state is still limited. The difficulty in interpretation of ^1H NMR data of low-moisture samples is usually associated with structural complexity of samples with corresponding heterogeneous proton environments. This will give rise to a complicated proton NMR signal. The results presented here have been acquired using instrumentation that is particularly well suited to characterizing the very broad spectral components typically encountered in low-moisture starch samples. Although low-field time-domain NMR does have some advantage over high-resolution NMR (e.g., it is inexpensive), high-resolution NMR can provide valuable information and cannot be replaced by low-field time-domain NMR in some aspects (e.g., line shape analysis). Hence, the objective of this research is to study the water and solids (starch) mobility as monitored by ^1H NMR relaxation times (T_2^*, T_2, and T_1) and to study the dynamics of these parameters in waxy corn starch over the water content ranges from 10.5 to 25.6% at 25 °C. This type of information will provide a better understanding of the role of water and solids mobility and glass transition in controlling food stability.

MATERIALS AND METHODS

Sample Preparation. Waxy No.1 corn starch (A. E. Staley Mfg. Co., Decatur, IL) was dried in a vacuum oven (29 in. of Hg and 60 °C for 24 h; AOAC, 1990). The dried sample was then equilibrated at 25 °C against various saturated salt solutions of known a_w (0.33−0.97) using the proximity equilibrated cell method (Lang et al., 1981). Moisture contents of equilibrated samples were calculated in duplicate by changes in the weight of the samples. The experimental error for the equilibrated moisture content was in the order of ±0.3%, and only the average values are presented. The moisture sorption isotherms of all samples were done at 25 °C by adsorption.

NMR Analysis. A Bruker MSL 300WB NMR spectrometer (Bruker Instruments, Inc., Billerica, MA), operating at 300.122 MHz proton resonance frequency, was used to obtain the wide-line ^1H NMR spectra. Approximately 300 mg of each sample was packed into a 7-mm polymer (zirconia) rotor. All measurements were done in duplicate at 25 °C. The spectra were acquired using a spectral width of 125 kHz. The large spectral width was necessary to observe both the broad component of the immobile protons and the narrow component of the mobile protons in the samples (Hills et al., 1991; Tanner et al., 1991; Wu et al., 1992; Li et al., 1998).

Effective Spin−Spin Relaxation Time (T_2^*). A one-pulse experiment was used to measure the effective spin−spin

relaxation times (T_2^*, s) of the samples. A 90° ^1H pulse (5 μs) and a preacquisition delay time of 2.5 s were used to obtain the spectra of samples. The spectrum of each sample was then decomposed into broad and narrow components and fitted to a sum of two simple line shape functions of Lorentzian or Gaussian. It was found that both Lorentzian and Gaussian functions give close values on peak height and half-height line width for each spectrum based upon a nonlinear least-squares curve-fitting ($r^2 \sim 0.9$). To calculate T_2^* values (based upon the line width at half-height peak), we took the approach of Lorentzian line shape, which is what was normally assumed in this excerise. The areas of broad and narrow components and the line width ($\nu_{1/2}$, s^{-1}) at half-height of each component were measured using Peakfit software (Jandel Scientific, San Rafael, CA). T_2^* was then calculated from the line width at half-height of each component by the following equation (Derome, 1987):

$$T_2^* \text{ (s)} = 1/\pi\nu_{1/2} \text{ (s}^{-1}) \tag{1}$$

Spin−Spin Relaxation Time (T_2). T_2 was measured using a Carr−Purcell−Meiboom−Gill (CPMG) pulse sequence (90°−τ−180°−τ−τ−180°−τ−acquisition), which measured the attenuation of the echo with increasing delay time (τ). The 90° and 180° pulse widths were 5 and 10 μs, respectively. Ten τ values (ranging between 5 and 500 μs) were used for each T_2 determination. The preacquisition delay time was set to 2.5 s. T_2 was calculated by fitting data to the equation

$$\ln I_t = \ln I_0 - t/T_2 \tag{2}$$

where I_0 is the peak height of the echo at time $t = 0$, and I_t is the peak height of the echo at time t (the number of echoes is two in this case; therefore, $t = 4\tau$). A plot of $\ln I_t$ against t yields a straight line, which has a slope equal to $-1/T_2$. Linear curve fitting was done using SigmaPlot software (Jandel Scientific).
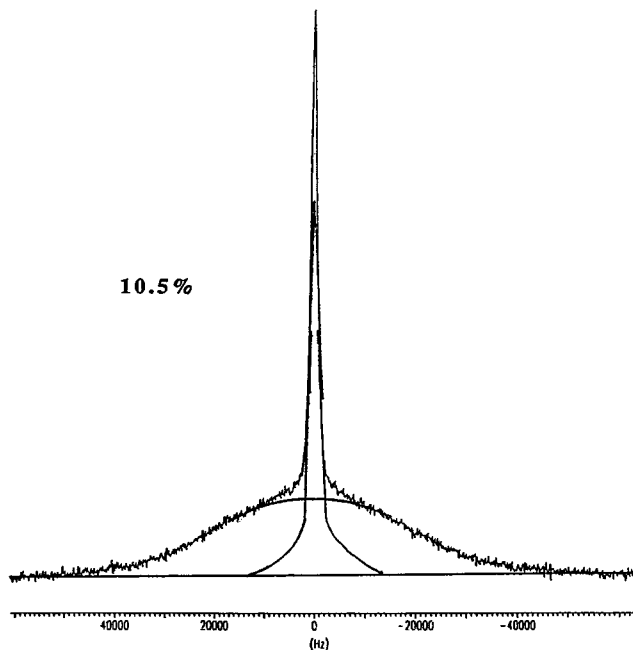
Spin−Lattice Relaxation Time (T_1). T_1 was measured using the inversion−recovery pulse sequence ($5T_1$−180°−τ−90°−acquisition) (Vold et al., 1968). The 90° and 180° pulse widths were 5 and 10 μs, respectively. The preacquisition delay time was set to 2.5 s. Ten τ values (ranging between 50 and 1 s) were used for each T_1 determination. The 10 spectra of each sample were then decomposed into broad and narrow components, and the peak height of each component was measured by using Peakfit software (Jandel Scientific). T_1 was calculated by fitting data to the equation

$$\ln(I_0 - I_t) = \ln(2I_0) - t/T_1 \tag{3}$$

where I_0 is the maximum measurable peak height (at time $t = 0$, immediately after the 180° pulse, $I_t = -I_0$) and I_t is the peak height at time $t = \tau$. A plot $\ln(I_0 - I_t)$ against t yields a straight line, which has a slope equal to $-1/T_1$. Linear curve fitting was done using SigmaPlot software (Jandel Scientific).

RESULTS AND DISCUSSION

Simultaneous Observation of Mobile and Immobile Protons. The wide-line ^1H NMR spectrum for waxy corn starch of 10.5% water content at 25 °C with the line shape obtained by summing two simple line shape functions is shown in Figure 1. The main features include a complex broad proton component upon which is superimposed a narrow proton component. The best-fit combination of simple line shape functions was a broader Lorentzian (82 kHz, 80.2% of total peak intensity) and a narrower Lorentzian (2.6 kHz, 19.8%), as shown in Figure 1. For starch samples containing up to 25.6% water, an increase in sorbed water results in an increase in the relative intensity of the narrow component and a decrease in the relative intensity of the broad component (Figure 2). A progressive decrease

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Figure 1. Wide-line ^{1}H NMR spectrum for waxy corn starch of 10.5% water content with the line shape obtained by summing two simple line shape functions.
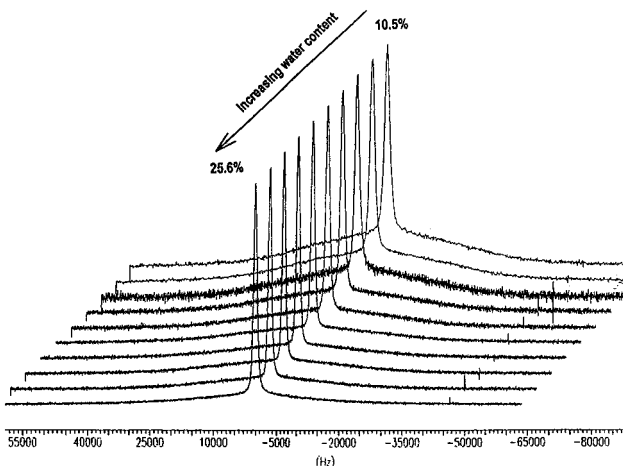
Figure 2. Wide-line ^{1}H NMR spectra for waxy corn starch of various water contents.

in ^{1}H NMR line width was also observed for both the broad component (from 82 to 69 kHz) and the narrow component (from 2.6 to 1.6 kHz) as water content increased from 10.5 to 25.6%. The broad component corresponds to an on-resonance free induction decay (FID) that has decayed within tens of microseconds, whereas the decay of magnetization associated with the narrow component of the line shape is much longer. Although some spectra of hydrated starch have been published, most studies have tended to ignore the broader line shape component. This is probably due to the difficulties encountered in recording the initial fast decaying part of the FID.

Owing to the structural complexity of starch, the decay of magnetization is complex and cannot always be decomposed unambiguously into two components: a fast decay ascribed to the more rigid starch protons and a slow decay associated with the water protons. Leung et al. (1976) studied the mobility of water in corn starch using ^{1}H NMR. It was found that the ^{1}H NMR $T_2{}^{*}$ values showed single-exponential decay for samples
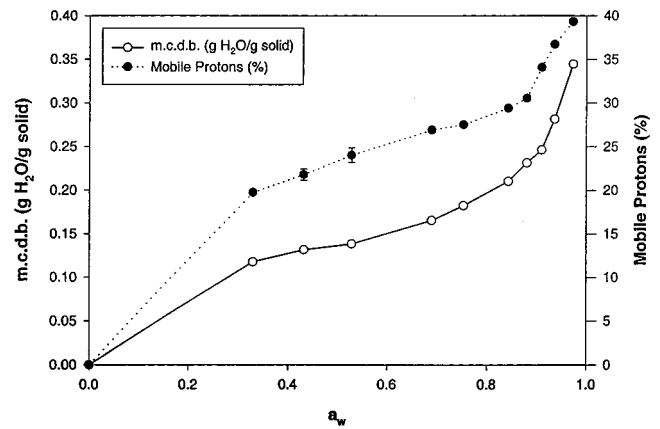
Figure 3. Moisture sorption isotherm and percentages of mobile protons for waxy No. 1 corn starch.

containing <45% water content and multiphase behavior at higher water content. Three types of protons are expected in low-moisture starch samples, namely, water protons, nonexchangeable starch protons (CH), and exchangeable hydroxyl protons (COH). However, as samples contain <35 wt % of water, there is no bulk water phase and greatly reduced proton-exchange rates are expected (Hills et al., 1991). Therefore, at fixed temperature, the observed increase in intensity of the narrow component with increase in water content suggests that the narrow component is dominated by the water. Tanner et al. (1991) attempted to replace all OH groups with OD groups by D_2O exchange with waxy maize starch samples and found that the intensity of the narrow component decreases significantly. This further supports the assumption that the narrow line shape component arises predominantly from water protons.

The moisture sorption isotherm of waxy No.1 corn starch, plotted as moisture content (grams of H_2O per gram of solid) versus a_w is shown in Figure 3. The isotherm shows a typical food moisture sorption isotherm, which is sigmoid in shape. Percentages of mobile protons for waxy No.1 corn starch over the a_w range from 0.33 to 0.97, at 25 °C, were measured and are also plotted in Figure 3. The mobile proton signal intensity increased from 19.8 to 39.3% over the a_w range from 0.33 to 0.97 (i.e., 10.5−25.6% water content). The percentage of mobile protons was measured by integration of the narrow component in the wide-line ^{1}H NMR spectrum. In this case, both starch and water protons could contribute to the ^{1}H signal. However, the mobile proton signal intensity showed a pattern similar to that of the moisture sorption isotherm (Figure 3). Moreover, line shape analysis of the broad and narrow components gives a ratio of protons in the two components that corresponds approximately to the known water contents of the different samples. For a sample with 10.5% water, the integrated ratio (using Figure 1 data) and the calculated ratio of the broad resonance area to the narrow resonance area were approximately 2.97 and 2.95, respectively. The calculated ratio was based upon each mole of water having two protons and each mole of starch monomer having seven nonexchangeable protons. In another study of waxy maize starch containing 10% water by solid-echo experiment, it was found that a distinct echo is observed with the second 90° pulse applied in the fast-decaying part of the FID, whereas no clear echo occurs when the second pulse is applied
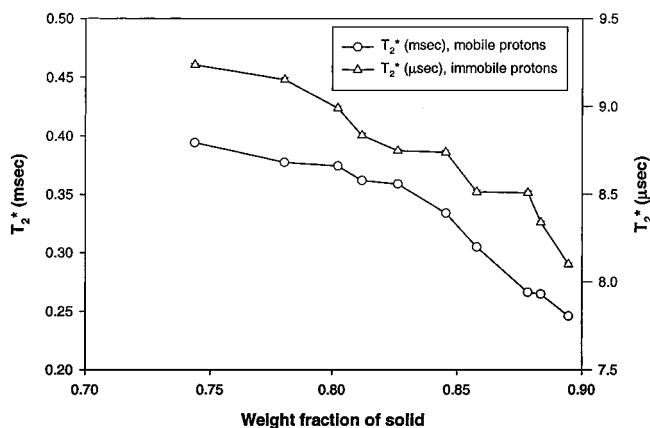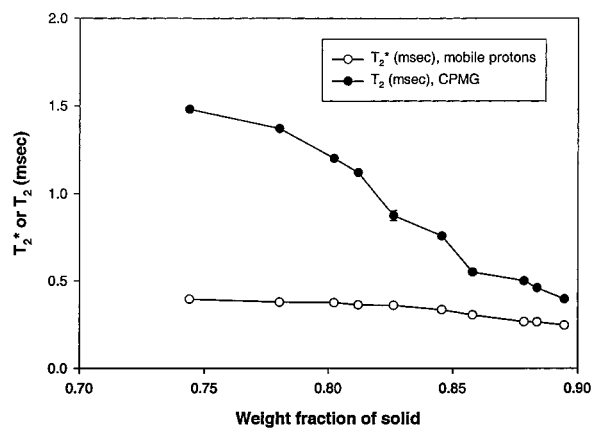
Figure 4. ^{1}H NMR effective spin−spin relaxation time (T_2^*) as a function of solid concentration for waxy No. 1 corn starch.

Figure 5. ^{1}H NMR T_2 and T_2^* of mobile protons as a function of solid concentration for waxy No. 1 corn starch.

in the more slowly decaying part of the FID (Tanner et al., 1991). This, together with the observed distinct narrower line width (1.6−2.6 kHz) of the narrow proton component as compared to the broader line width (69−82 kHz) of the broad proton component, suggests that the spectrum was a superposition of protons from the mobile water phase (mobile protons) and rigid starch phase (immobile protons) in the systems.

Li et al. (1998), investigating the mobility of "unfreezable" and "freezable" water in waxy corn starch using ^{2}H and ^{1}H NMR, found that majority of water molecules exhibited a distinctly higher mobility than starch molecules. In the case of the ^{2}H NMR data, there was 84% mobile D_2O present at 14% total D_2O content and 90% mobile D_2O present at 21.4% D_2O sample. In the case of the ^{1}H NMR data, the measured mobile proton matched well with the calculated values in the samples and the proton from the water molecules dominated the narrow proton signal. These studies again support our earlier conclusion that water was mobile in the highly rigid starch matrix in the solid and semisolid states.

Wide-Line ^{1}H NMR Relaxation Times Studies. The ^{1}H NMR effective spin−spin relaxation time ($T_2^* = 1/\pi\nu_{1/2}$) as a function of solid concentration for the waxy No. 1 corn starch samples is shown in Figure 4. For both broad and narrow components, the T_2^* values decreased with increasing solid concentration (Figure 4). This indicates that the molecular mobility in waxy No. 1 corn starch samples successively decreased with increasing solid concentration. Moreover, the T_2^* values of narrow proton components are at the millisecond scale, whereas the T_2^* values of broad proton components are at the microsecond scale. This result indicated that wide-line ^{1}H NMR spectroscopy is able to separate modes and quantitate the magnitude of molecular mobility for each component in complex systems. The distinct narrow and broad components also indicate that water was mobile in the starch matrix despite the starch molecules being in the solid and semisolid states.

The spectrum together with measurements of half-height line width ($\nu_{1/2}$, s^{-1}) shows that a narrowing of the broad spectral component occurs on addition of water to the sample. Because proton exchange is slow in the low-moisture regime, this effect is not a consequence of proton exchange but indicates that water is causing an increase in the starch mobility. For starch samples with 21.9% water, the narrow component is very intense, whereas the broad spectral component has narrowed significantly. The motional narrowing ob-

served in this study occurs when a correlation time (τ_c) for starch motion falls within the range (Abragam, 1989)

$$(\omega_o)^{-1} < \tau_c < (M_2)^{-1/2} \qquad (4)$$

where M_2 is the second moment of the proton line shape. Usually M_2 is estimated by

$$M_2 \approx (\nu_{1/2}/1.18)^2 \qquad (5)$$

As the rigid-lattice half-height line width ($\nu_{1/2}$) of waxy corn starch is ∼35 kHz, the motional narrowing regime for waxy corn starch falls in the range $5.3 \times \sim10^{-10} < \tau_c$ (s) $< 5.4 \times 10^{-6}$. The onset of significant motional narrowing occurring in waxy corn starch samples containing >20% water is consistent with the known glass transition temperature (T_g) for starch. To observe a T_g at room temperature (e.g., 25 °C), starch samples must contain ∼20% water by weight (Zeleznak and Hoseney, 1987). Starch is semicrystalline but contains significant amounts of amorphous materials. The crystallites in starch samples are hydrated, and the extent of crystallinity increases typically with the addition of water to starch samples. It is interesting to note that the increase in mobility of the starch chains on hydration accompanies an increase in sample crystallinity (Tanner et al., 1987; Roos and Karel, 1991). This may be due to water acting as a plasticizer, allowing starch chain motions to remove strain and hence the defect within the starch samples.

The ^{1}H NMR spin−spin relaxation times (T_2) were obtained using a CPMG pulse sequence. Due to the increasing delay time involved in the experiment, the initial fast decaying part of the FID cannot be recorded. Therefore, the resulting spectrum showed only the narrow proton component. The calculated T_2 values are at the millisecond scale the same as the T_2^* values of the narrow proton components. The ^{1}H NMR T_2 and T_2^* values of mobile protons as a function of solid concentration for the waxy No. 1 corn starch samples are shown in Figure 5. The T_2 values show the same trend as T_2^* values, a decrease in T_2 values with increasing solid concentration (Figure 4 and 5). The T_2 is related to the composite T_2^* by the following equation (Kemp, 1986):

$$1/T_2^* = 1/T_2 + 1/T_2^{\text{inhom}} \qquad (6)$$

The second term on the right-hand side describes the
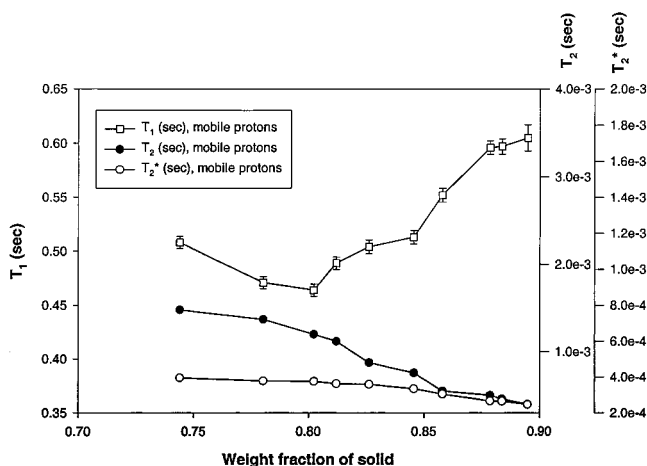
Figure 6. ^{1}H NMR T_1, T_2, and T_2^* of mobile protons as a function of solid concentration for waxy No. 1 corn starch.
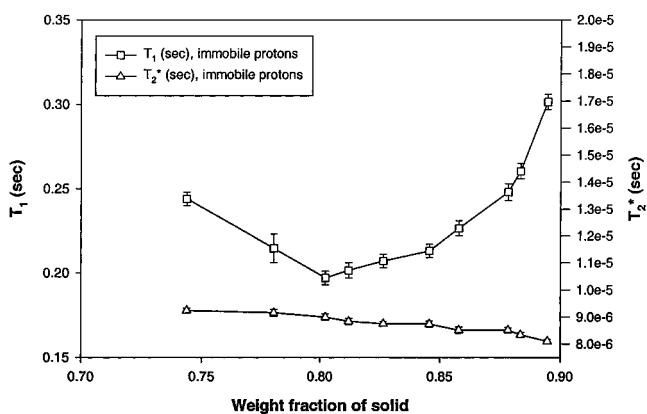
Figure 7. ^{1}H NMR T_1 and T_2^* of immobile protons as a function of solid concentration for waxy No. 1 corn starch.

effect of inhomogeneties in the sample and magnetic field. Therefore, how close T_2 is to T_2^* depends on the magnitude of these inhomogeneties. The CPMG experiment reveals a real T_2 that is much larger than the T_2^* calculated from the half-height line width. It was observed that the difference between T_2 and T_2^* values of mobile protons increases with decreasing solid concentration (Figure 5). The observed large T_2 values at low solid concentrations may be attributed to the increasing mobility with amounts of water in the samples. The small T_2 values, in the entire concentration range studied, are probably due to dipole−dipole interaction in a semirigid environment.

The ^{1}H NMR T_1 (spin−lattice relaxation times), T_2, and T_2^* of mobile protons as a function of solid concentration for the waxy No. 1 corn starch samples are shown in Figure 6. The ^{1}H NMR T_1 and T_2^* of immobile protons as a function of solid concentration for the waxy No. 1 corn starch samples are shown in Figure 7. The spin−lattice relaxation decay was found to be a single exponential for all starch samples studied. Figures 6 and 7 show the general pattern expected for T_1 and T_2 versus τ_c (Bloembergen et al., 1948). Addition of water to the dried starch samples (i.e., decreasing solid concentration) results in a decrease in the T_1 of both narrow and broad components and gives rise to a distinct "T_1 minimum" for both (Figures 6 and 7). This indicates that water provides a relaxation path for the starch protons. Tanner et al. (1991), investigating the T_1 of waxy maize starch containing 18% D_2O, found no corresponding T_1

minimum, and the T_1 values obtained from this sample are similar to those of dried samples in the higher temperature range studied. The results again indicate that the reduction in the relaxation times of the starch samples containing ordinary water occurs primarily as a consequence of the water motion rather than through the mobility of starch.

The spin−lattice relaxation is most rapid at the T_1 minimum, where the solid fraction of the starch sample is between 0.802 and 0.791 (i.e., between 19.8 and 21.9% water content), whereas spin−spin relaxation successively increased in rate with increasing solid concentration. For starch samples containing <20% water, the value of T_1 increases with an increase in solid concentration. This is expected for solid samples in the rigid-lattice regime. In the rigid-lattice regime, spin−lattice relaxation is slow, the lifetime of the individual spin state is short because the excitation passes via mutual spin−flips to other spins. Therefore, T_1 is long but T_2 is short and the NMR signals are broad as a result of the short T_2. The observed T_1 minimum occurring in waxy corn starch samples, at 25 °C, containing >20% water is again consistent with the known glass transition temperature (T_g) for starch.

There are potentially three types of water motion that could cause the water to act as a spin−lattice relaxation source for the low-moisture starch samples. These are the fast averaging of the intramolecular dipole−dipole interaction characterized by the fast correlation time τ_f, the slower averaging of the residual dipolar interactions characterized by a longer correlation time τ_s, and the diffusion of the water between sites characterized by the mean residence time τ_e. Of these motions, the fastest is expected to be the one most effective in causing spin−lattice relaxation, and this is probably the near-isotropic water reorientation with the correlation time τ_f. If this is the case, an approximate magnitude for τ_f can be derived from the well-known condition that at the T_1 minimum $\omega_o\tau_f = 0.6158$ (Abragam, 1989). For waxy corn starch containing 19.8% water, this gives $\tau_f \approx 10^{-10}$ s at 25 °C. The motion responsible for the T_1 minimum arises from the motion of the water molecules with a correlation time $\tau_f \approx 10^{-10}$ s. This indicated that for waxy corn starch samples with 19.8% water, the water is moving relatively quickly even when samples are in the glassy state (see below).

Water Is Mobile in the Glassy State. It has been recognized that the amorphous regions of starch undergo a glassy transition at a temperature T_g that depends on water content (Zeleznak and Hoseney, 1987; Levine and Slade, 1988; Roos and Karel, 1991; Slade and Levine, 1993). The T_g values of waxy corn starch with various water contents were calculated using the Gordon−Taylor equation

$$T_g = (W_1 T_{g1} + k W_2 T_{g2})/(W_1 + k W_2) \qquad (7)$$

where subscripts 1 and 2 refer to the two components. W_1 is the weight fraction of component 1, W_2 is the weight fraction of component 2, and respective glass transition temperatures are T_{g1} and T_{g2}. k is an empirical constant. The Gordon−Taylor equation has been used as a predictor of glass transition temperatures of binary mixtures of solids and water (Roos and Karel, 1991; Kalichevsky et al., 1993; Kou et al., 1999). T_g values used in the calculations were −135 °C (138 K) for pure water and 243 °C (516 K) for anhydrous starch; constant k used in the calculations was 5.2 (Roos

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and Karel, 1991). According to the calculated T_g values of these starch samples, the two starch samples (21.9 and 25.6% water contents) had T_g values below the experimental temperature of 25 °C. This suggests that the two starch samples have greater molecular mobility (i.e., in the viscous rubbery state) compared to the other starch samples of the water contents ranging from 10.5 to 19.8% (i.e., in the glassy state).

^{1}H NMR relaxation times were correlated with the calculated T_g values for all starch samples. The T_2^* and T_2 values of mobile protons and the T_2^* values of immobile protons decrease progressively with increasing solid concentrations and show a "break point" in the concentration range between 19.8 and 21.9% water content (Figures 4 and 5). The observation of the narrow component suggests that very rapid motion is responsible for the averaging of the major fraction of the dipolar interactions for the protons associated with the narrow spectral component. This also indicates that the narrow spectral component arises predominantly from water and the absorbed water molecules are undergoing relatively fast motion. This agrees with the previous conclusion of $\tau_f \approx 10^{-10}$ s: water is mobile in the extremely high rigidity of starch matrix in the glassy state. The T_1 minimum was observed between 19.8 and 21.9% water of samples for both mobile and immobile protons (Figures 6 and 7). This concentration range, which shows a break point for T_2 and T_2^* and a T_1 minimum, is the same concentration range for starch samples to change from the glassy to the viscous rubbery state. This indicated that wide-line ^{1}H NMR relaxation times (i.e., T_2^*, T_2, and T_1) may be useful as indicators of glass transition for starch samples in the solid state.

The relationship between NMR relaxation times and glass transitions in food materials remains to be elucidated. Kalichevsky and Blanshard (1992) studied the glass transition of amylopectin by recording the ^{1}H NMR FID after a 90° pulse. The fast decay (rigid) component, with T_{2R}, corresponds to solid polysaccharide protons in the glass or crystalline states, whereas the slow (mobile) component, with T_{2M}, reflects water protons and exchangeable protons. After the rigid lattice limit (RLL), the increase of T_{2R} with temperature is attributed to the onset or increase in frequency of the motion of groups containing hydrogen. The RLL determined by NMR was found to be 20−30 °C lower than the T_g measured by DSC. The thermal results also suggest an increase of T_g with crystallinity, whereas NMR shows an initial difference between amorphous and 2% crystalline samples but no difference between 2 and 4% crystalline samples. Kalichevsky and Blanshard suggest that this is because NMR looks at short-range mobility, whereas DSC and DMTA look at larger scale effects. A detailed investigation of water dynamics in 10% maltose glasses using ^{1}H and ^{2}H NMR reported a similar increase in the maltose proton relaxation time above the glass transition temperature and, in addition, demonstrated the remarkable mobility of water in the glassy state of the 10% maltose glasses (Hills and Pardoe, 1995). On the basis of these water relaxation data, a model of the glass state has been suggested in which water molecules undergo rapid rotational and translational motions inside more rigid "cages" or "channels" formed by maltose molecules (Gil et al., 1996).

The difference between measuring the glass transition temperature (T_g) with NMR spectroscopy versus DSC

should be noted. The T_g values obtained using DSC are based on polymer motions at the macroscopic level and attempts to characterize the overall mobility of the system. The T_g determination using NMR spectroscopy is based on polymer motions at the microscopic level and measures the molecular mobility of the system. In NMR spectroscopy, the influence of the glass transition on molecular motions of individual components can be also observed. Furthermore, an improved understanding of molecular motions of individual components above and below the glass transition temperature can serve to better the understanding of the property of the glass transition itself.

Summary. The mobility (dynamics) of the water and solid components in waxy corn starch samples was studied by wide-line ^{1}H NMR. The ^{1}H NMR T_1, T_2, and T_2^* values were obtained using the inversion−recovery pulse sequence, the CPMG pulse sequence, and the half-height line width multiplied by π, respectively. It was observed that the spectrum of each sample includes a complex broad proton component upon which is superimposed a narrow proton component over water content from 10.5 to 25.6% at 25 °C. The result indicated that the proton from the water molecules dominated the narrow proton resonance and the proton from the starch molecules dominated the broad proton resonance. The ^{1}H NMR relaxation times were correlated with the calculated T_g values for all starch samples. The T_2^* and T_2 values decrease (i.e., decreasing mobility) with increasing solid concentration and show a break point in the concentration range between 19.8 and 21.9% water content of sample. The T_1 shows a T_1 minimum in the same concentration range. This concentration range is the same concentration range for starch samples to change from the glassy to the viscous rubbery state. This demonstrates that wide-line ^{1}H NMR relaxation times (i.e., T_2^*, T_2, and T_1) may be useful as indicators of glass transition for starch samples in the solid state. The observation of the narrow component together with the fast correlation time ($\tau_f \approx 10^{-10}$ s) of water molecules indicates that the narrow spectral component arises predominantly from water and the absorbed water is mobile in the extremely high rigidity of starch matrix in the glassy state.

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