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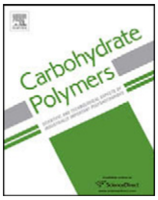

State of water in starch–water systems in the gelatinization temperature range as investigated using dielectric relaxation spectroscopy

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ABSTRACT

The dielectric response of native wheat starch–water slurries containing 5–60% starch (w/w) was measured in the frequency range of 0.2–20 GHz after heating the slurries to 7 different temperatures between 25 and 90 °C for 30 min. Three relaxations, with relaxation time range of 4–9 ps, 20–25 ps and 230–620 ps at 25 °C, were identified from the dielectric spectra of starch slurries. The fastest relaxation process (4–9 ps) was attributed to bulk water while the two slower relaxations were attributed to the confined water molecules present in the starch–water system. The amount of water exhibiting the slowest relaxation (230–620 ps) was calculated to be 0.08–0.16 g water/g starch, which was close to the monolayer water associated with wheat starch. Mobility of bulk water was significantly reduced ($P < 0.001$) upon gelatinization at low starch concentration (10% starch), but remained unaffected at higher starch concentrations. The mobility of two slower relaxing water species was not significantly influenced ($P > 0.19$) by gelatinization at all starch concentrations.

1. Introduction

Starch gelatinization is an irreversible order-to-disorder phase transition which occurs when starch granules are heated in the presence of water (Donovan, 1979; Jenkins & Donald, 1998). Gelatinization influences the texture, digestibility and shelf-life of several food products such as bread, cereals and pasta products. The physico-chemical events occurring during gelatinization, i.e. granular swelling, crystallite melting and viscosity development are governed by the amount of water available to the starch granules. In fact, starch–water interactions are key to developing a mechanistic understanding of the gelatinization process (Baks, Ngene, van Soest, Janssen, & Boom, 2007; Waigh, Gidley, Komanshek, & Donald, 2000).

Several models have been proposed to explain the differences in the gelatinization mechanisms in excess and intermediate water conditions (Evans & Haisman, 1982; Slade & Levine, 1988; Waigh et al., 2000). In the presence of excess water (>70% w/w), progressive heating of the starch granules weakens the stabilizing hydrogen bonding forces inside the granule resulting in water penetration and granular swelling (Parker & Ring, 2001). Continued swelling disrupts the ordered radial orientation of the amylopectin chains and results in loss of native crystalline order due to the hydration-facilitated melting of the crystallites (Buleon & Colonna, 2007). At intermediate water concentrations (30–70% w/w), there is not enough water for the hydration of all the starch granules, which broadens the temperature range of gelatinization (Biliaderis, 2009; Parker & Ring, 2001). Thus, in contrast to the excess water conditions where gelatinization results in a single DSC endothermic peak (referred to as G), two endothermic peaks (referred to as G and M1) are observed at intermediate water concentrations (Donovan, 1979).

Starch–water interactions have mainly been studied using ^{1}H, ^{2}H and ^{17}O Nuclear Magnetic Resonance (NMR) and differential scanning calorimetric (DSC) techniques. ^{1}H NMR spectroscopy revealed two populations of water molecules, described as bound and weakly bound water, in wheat starch–water suspensions (Le Botlan, Rugraff, Martin, & Colonna, 1998). Later Tang, Godward, and Hills (2000), using ^{2}H NMR techniques, showed the existence of at least three water populations in potato starch–water systems, which were assigned to water molecules in the amorphous growth regions, semi-crystalline lamellae, and channel water inside the hexagonal channels of amylopectin crystal clusters. Tananuwong and Reid (2004) investigated the extent of starch–water interactions by determining the amount of additional unfrozen water (AUW) using DSC. While these studies have improved the understanding of starch–water interactions, the effect of water content on the change in water mobility during gelatinization is still not well understood.

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Dielectric relaxation spectroscopy (DRS) is a widely used method to study biopolymer–water interactions (Mashimo, 1997; Pissis, 2005). Dielectric relaxation monitors the motion of a molecular ensemble by measuring the response of the total dipole moment of the ensemble to an externally applied electric field (Schönhals & Kremer, 2003). Water molecules, owing to their dipolar nature, undergo orientational polarization and exhibit dielectric relaxation in the microwave frequency region (Ellison, Lamkaouchi, & Moreau, 1996; Von Hippel, 1988). This relaxation is characterized by a peak in the dielectric loss (ε'') and a step-like decrease in the dielectric constant (ε'). In the presence of biopolymers such as starch, a fraction of water molecules are confined such that their mobility is slowed down due to the restraining effect of the physical matrix (Hayashi, Shinashiki, & Yagihara, 2002; Ryabov, Feldman, Shinyashiki, & Yagihara, 2002). These water molecules exhibit slower relaxations as compared to the bulk water molecules (Mashimo, 1994).

Dielectric relaxation has the potential to elucidate important facets of starch–water interactions during starch gelatinization. Most of the previous studies have focused on the relaxation processes occurring in starch polymers, and hence starch–water systems with <15% moisture (w/w) have been used (Butler & Cameron, 2000; Einfeldt, Meiβner, Kwasneiwski, & Einfeldt, 2001; Laredo, Newman, Bello, & Mueller, 2009; Majumder, Meißner, & Schick, 2004; Ono, Kuge, & Koizumi, 1958a; Ono, Kuge, & Koizumi, 1958b). This ruled out the effects of granule swelling occurring during gelatinization. In the presence of relatively higher moisture (33–46% w/w), wheat starch–water systems exhibited six relaxations in the frequency range of 10^{-3}–10^{6} Hz and temperature range of −90 °C to 80 °C. These relaxations were assigned to the different kinds of motions in starch polymeric chains (Majumder, Meiβner, Schick, & Roy, 2006). Dielectric spectra of starch–water systems at progressive levels of hydration from 0.5 to 50% water at room temperature showed the presence of up to three relaxations in the frequency range of 10^{1}–10^{10} Hz (Abadie, Charboneirre, Gidel, Girard, & Guilbot, 1953). In our previous study (Motwani, Seetharaman, & Anantheswaran, 2007), we reported that dielectric constant of 20% starch slurries at 2450 MHz could be used to monitor the degree of corn starch gelatinization. In this study, we present a detailed investigation of the state and mobility of water in the starch–water systems in the gelatinization temperature range using dielectric relaxation spectroscopy in the frequency range of 0.2–20 GHz.

2. Materials and methods

2.1. Dielectric measurements

Native wheat starch (Midsol™ 50, MGP Ingredients, Atchison, KS) and deionized water were used to prepare starch slurries with 7 different concentrations between 5 and 60% starch (w/w, dry basis). The slurries were hydrated and mixed for 1 h at room temperature and then deaerated for 30 min using a peristaltic pump (Masterflex I/P, Cole Palmer, Vernon Hills, IL). The deaerated slurries were placed in specifically designed 15 ml jacketed beakers (28 mm ID, 25 inside height) connected to a circulating water bath (Model 9105, Polyscience, Niles, IL) and heated to seven different temperatures between 25 and 90 °C for 30 min. The dielectric response of the heated suspensions was measured using a vector network analyzer (Agilent/HP 8510C, Palo Alto, CA) using a coaxial cable connected to a dielectric probe (HP 85070B, Hewlett Packard Co., Santa Rosa, CA). The network analyzer was calibrated using air, metallic short, and deionized water at 25 °C and a frequency sweep was performed to obtain dielectric constant and dielectric loss factor data at 400 linearly spaced frequency points between 0.2 and 20 GHz. The dielectric constant and the loss factor values were calculated by the software provided by the manufacturer (Agilent 85070 E, Palo Alto, CA).

The dielectric response at 25 °C was measured for all the concentrations but only 10%, 30% or 50% suspensions were used to measure the dielectric response at elevated temperatures. Fresh samples were used for each measurement. The dielectric measurements were randomized and three independent replicates were performed for each temperature and concentration.

2.2. Analysis of dielectric spectra

The measured dielectric response of the starch–water systems was deconvoluted into separate relaxations using multi-step Debye spectral function expressed as,

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{1 + i\omega\tau_j} - i\frac{\sigma_{dc}}{\varepsilon_0\omega} \tag{1}$$

where $\varepsilon^*(\omega)$ is the relative complex permittivity, n are the number of separable relaxations in the measured frequency range, σ_{dc} is the direct current (DC) conductivity, ε_0 is the permittivity of free space, and $\Delta\varepsilon_j$ and τ_j are the dielectric relaxation strength and relaxation time, respectively, of the jth relaxation process (Kao, 2004; Schönhals & Kremer, 2003). The real and the imaginary parts of the complex relative permittivity in Eq. (1) could be expressed as (Asami, 2002),

$$\varepsilon'(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{1 + (\omega\tau_j)^2} \tag{2}$$

$$\varepsilon''(\omega) = \sum_{j=1}^{n} \frac{\Delta\varepsilon_j(\omega\tau_j)}{1 + (\omega\tau_j)^2} + \frac{\sigma_{dc}}{\varepsilon_0\omega} \tag{3}$$

The experimental data for the dielectric constant and dielectric loss, obtained as a function of frequency, were fitted to Eqs. (2) and (3) simultaneously using non-linear least squares regression using GraphPad Prism ver 4 (GraphPad Softwares Inc., La Jolla, CA). To obtain a quantitative estimate of the goodness of the fit, the normalize variance, S_N^2, was measured as,

$$S_N^2 = \frac{1}{N - P - 1}\left[\sum_{j=1}^{N}\left(\frac{\delta\varepsilon'(\omega_j)}{\varepsilon'_{\max}}\right)^2 + \sum_{j=1}^{N}\left(\frac{\delta\varepsilon''(\omega_j)}{\varepsilon''_{\max}}\right)^2\right] \tag{4}$$

where N are the total number of measurement frequencies, P is the number of fitted parameters, $\delta\varepsilon'(\omega_i)$ and $\delta\varepsilon''(\omega_i)$ are the residuals for dielectric constant and loss, respectively. The parameters $\varepsilon'_{\max}$ and $\varepsilon''_{\max}$ in Eq. (4) are the maximum values of dielectric constant and loss factor, respectively, and functioned as the weighing factors (Fuchs & Kaatze, 2001; Lu, 2005).

2.3. Statistical analysis

Three independent replicates of the relaxation times and relative relaxation strengths (amount of water associated with each relaxation) were obtained at each concentration and temperature of measurement. A crossed design with starch concentrations (10%, 30%, 50%) and temperatures (25 °C, 40 °C, 50 °C, 60 °C, 70 °C, 80 °C, 90 °C) as fixed factors was used to analyze the relaxation parameters using analysis of variance at $\alpha = 0.05\%$ using the General Linear Model of Minitab software (ver 15.0, Minitab Inc., State College, PA). This was followed by post hoc analysis using Tukey's HSD test at $\alpha = 0.05\%$.

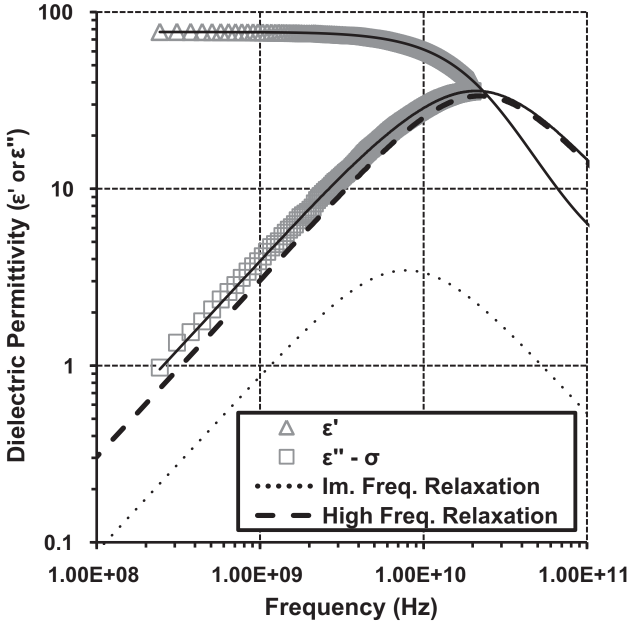

Fig. 1. Deconvoluted dielectric spectra of 10% starch slurry at 25 °C showing dielectric constant (ε') and dielectric loss factor (after removing the contribution due to dc conductivity) $(\varepsilon' - \sigma_{dc})$. The solid lines represent the best fit to the spectra obtained using Eq. (1).

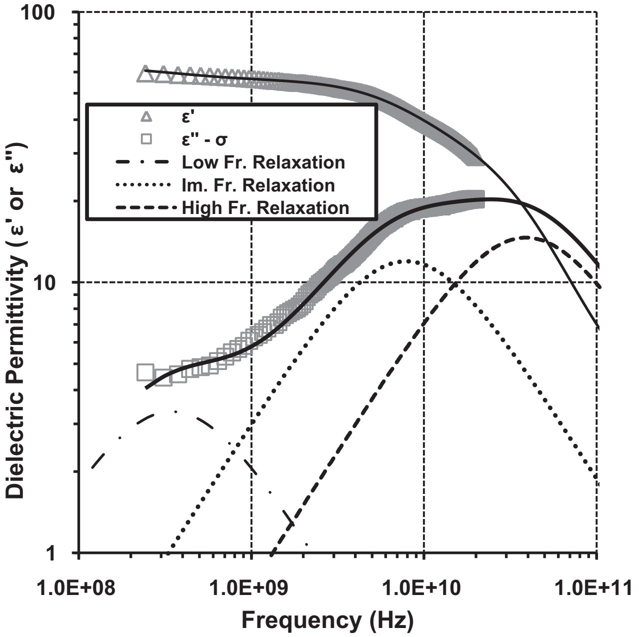

Fig. 2. Deconvoluted dielectric spectra of 50% starch slurry at 25 °C showing dielectric constant (ε') and dielectric loss factor (after removing the contribution due to dc conductivity) $(\varepsilon'' - \sigma_{dc})$. The solid lines represent the best fit to the spectra obtained using Eq. (1).

3. Results and discussion

3.1. Dielectric spectra of starch slurries

The dielectric spectra of slurries having ≤ 20% starch exhibited two relaxations ($j = 2$ in Eq. (1)), while at higher starch concentrations, three relaxations were observed ($j = 3$ in Eq. (1)). The relaxation times in the 10% starch slurry were 7.2 ± 0.03 ps and 19.7 ± 1.0 ps at 25 °C (Fig. 1), while those for 50% starch slurry were 5.2 ± 0.1 ps, 21.9 ± 0.2 ps and 524.8 ± 21.7 ps at 25 °C (Fig. 2). These relaxations will be referred to as high, intermediate and low frequency relaxations, respectively.

The relaxation time of the high frequency process (τ_h) was close to the relaxation time of pure water (8.28 ± 0.02 ps) and could be attributed to the rotational motion of bulk water molecules present in the starch–water system. This relaxation process denoted that the corresponding water molecules exhibited a behavior dominated by water–water hydrogen bonding and were located in regions where the local environment resembled bulk water.

The intermediate frequency relaxation was ∼2–4 times slower as compared to bulk water and molecules exhibiting this intermediate process were clearly more restrained as compared to bulk water. The presence of similar relaxation ($\tau = 23$ ps) in starch slurries with starch concentrations between 50 and 70% (w/w) has been reported previously as well (Abadie et al., 1953). The water molecules exhibiting intermediate frequency process were interacting with both bulk water and slower relaxing environments such as starch polymeric chains or highly confined water molecules associated with the starch granule.

The low frequency relaxation was observed only for higher starch concentrations (30% starch and above). This relaxation had a dielectric loss peak in the vicinity of 300–500 MHz at 25 °C and was weaker than intermediate and high frequency processes. Ours is the first study to report such a relaxation in starch–water systems. Low frequency relaxations in the MHz region are generally ascribed to highly confined water (Mashimo, Kuwabara, Yagihara, & Higasi, 1987; Miura, Yagihara, & Mashimo, 2003). These relaxations have been reported to occur in a variety of biomaterials such as globular proteins (Miura, Asaka, Shinyashiki, & Mashimo, 1994), gellan gum (Mashimo, Shinyashiki, & Matsumura, 1996), bovine serum albumin (Miura, Hayashi, Shinyashiki, & Mashimo, 1995), native and heat-denatured ovalbumins (Sun, Ishida, & Hayakawa, 2004), raw fish and chicken (Miura et al., 2003). These highly confined water molecules exhibit strong interaction with the starch polymers which could be attributed to hydrogen bonding. These water molecules are similar to monolayer water molecules described in the classic water binding regimes such as BET and GAB. To elucidate the nature of these water molecules, the amount of water exhibiting this relaxation was determined by investigating the effect of starch concentration on the dielectric response.

3.2. Effect of starch concentration on dielectric response

The effect of starch concentration on the relaxation times of high, intermediate and low frequency relaxations is shown in Fig. 3. The high frequency relaxation time (τ_h) of 5% starch slurry (8.6 ± 0.02 ps) was close to the relaxation time of pure water (8.28 ± 0.02 ps) (Kaatze, 1997) further confirming that this relaxation process was due to bulk water. The value of τ_h decreased upon increasing the starch concentration from 5% to 30%, indicating shifting of the loss peak to higher frequencies upon increasing the starch concentration. The relaxation behavior of bulk water is usually described in terms of the wait-and-switch model which relates the molecular motions of water to its structural properties (Kaatze, 2000). According to this model, dielectric relaxation time is controlled by the time for which a water molecule has to wait to reorient itself until a suitable site for formation of a new hydrogen bond exists. The reorientation process resembles switching and occurs within 0.1 ps (Behrends, Fuchs, Kaatze, Hayashi, & Feldman, 2006; Kaatze, 2000). The local concentration of hydrogen bonding abilities acts as a dominant influence on the reorientational behavior of water, and hence, dielectric relaxation of bulk water is described to be co-operative in nature (Ryabov et al., 2002). The presence of polymer in the polymer–water mixture reorganizes the water into specific cooperative structures which are influenced by

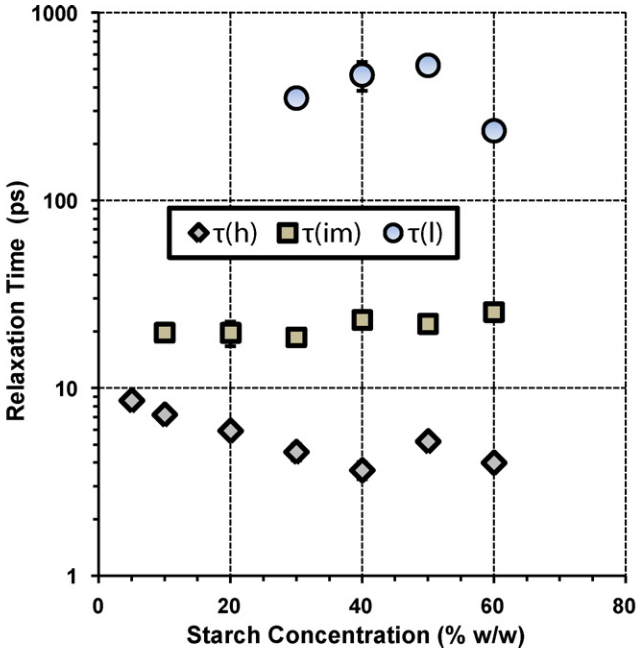

Fig. 3. Effect of starch concentration on high frequency (τ_h), intermediate frequency (τ_{im}) and low frequency (τ_l) relaxation times at 25 °C. Intermediate frequency relaxation was not observed in 5% starch slurry and the low frequency relaxation was not observed in slurries below 30% starch concentration. Error bars represent one standard deviation above and below the mean value.

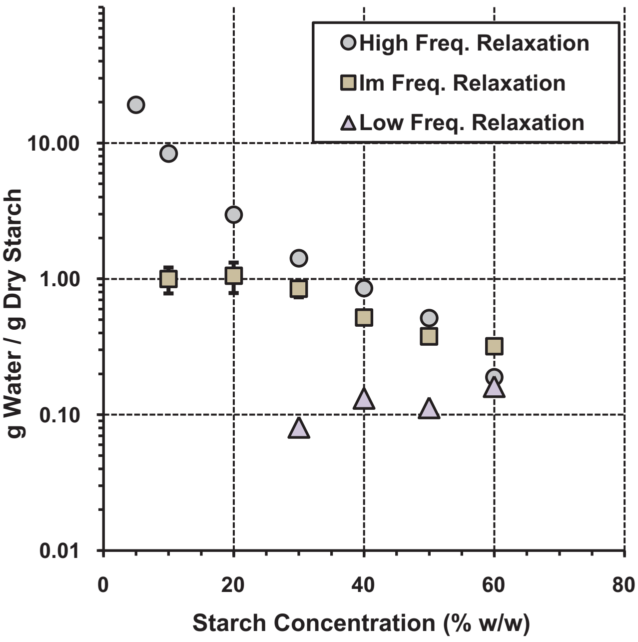

Fig. 4. Effect of starch concentration on the amount of water exhibiting high, intermediate and low frequency relaxations at 25 °C. The calculations for g water/g dry starch were performed using Eq. (6). Intermediate frequency relaxation was not observed in 5% starch slurry and the low frequency relaxation was not observed in slurries below 30% starch concentration. Error bars represent one standard deviation above and below the mean value.

the nature of the polymer (Ryabov et al., 2002). It could be hypothesized that starch polymeric chains reorganized the structure of water in a manner that concentration of hydrogen bonding sites in the vicinity of bulk water molecules increased which resulted in shorter relaxation times.

The intermediate frequency relaxation time (τ_{im}) was independent of starch concentration. Low frequency relaxation time (τ_l) increased with starch concentration from 30% to 50% starch. Further increase in starch concentration from 50% to 60% starch resulted in drop in the τ_l. Upon increasing the starch concentration to 60%, when starch–water system does not have a continuous medium of water, τ_l was expected to increase owing to additional resistance to the movement and orientation of water molecules in the presence of increased amount of starch polymers. Since each relaxation has a distinct activation enthalpy (Lu, 2005), it could be hypothesized that water molecules displaying low frequency relaxation were possibly exhibiting less dynamic exchange with the other water species. Increasing starch concentration resulted in higher number of water molecules exhibiting the low frequency relaxation and provided more opportunities for such water molecules to 'jump' to other sites without crossing the activation energy barrier. This possibly resulted in enhanced mobility and shorter relaxation time. In the literature, the reorientational motion of water molecules is assumed to follow an activated jump mechanism (Kaatze, 2000).

The effect of starch concentration on the dielectric relaxation strength of starch–water systems is shown in Fig. 4. Since water molecules were the only relaxing species in the starch–water system in the experimental frequency range, the relaxation strengths were normalized to g water/g dry starch. The calculations were performed based on the Kirkwood equation according to which the strength of a relaxation process is proportional to the number of molecules per unit volume, N_i, exhibiting the relaxation process:

$$\Delta\varepsilon_i = K(N_i) \tag{5}$$

where K is the proportionality constant which contains information regarding the relaxing species such as polarizability, dipole moment and Kirkwood correlation factor (Kao, 2004; Miura et al., 1994; Shinyashiki, Shimomura, Ushiyama, Miyagawa, & Yagihara, 2007). For a single relaxing species (water molecules in starch–water system) it is reasonable to assume that K remains constant for the different relaxation processes (Lu, 2005). Assuming that all the water molecules in the starch–water system were exhibiting dielectric response in the experimental frequency range, the expression for weight fraction of water molecules (w_j) exhibiting jth relaxation can be derived as (Motwani, 2009),

$$\frac{w_j}{w_s} = \frac{\Delta\varepsilon_j}{\sum_{j=1}^{n}\Delta\varepsilon_j}\cdot\frac{1-\Phi_s}{\Phi_s}\cdot\frac{1}{\rho_s} \tag{6}$$

where w_s is the weight fraction of starch, ρ_s is the density of starch, Φ_s is the starch volume fraction and $\Delta\varepsilon_j$ is the strength of the jth relaxation.

Increasing the starch concentration did not influence the amount of water exhibiting the low frequency relaxation. This suggested that water molecules exhibiting this relaxation were hydrogen bonded to the starch chains at the surface of the granules possibly representing the monolayer water. The intermediate frequency water could be hypothesized to be the multilayer water hydrogen bonded to the water molecules exhibiting low and high frequency relaxations. Water molecules exhibiting high frequency relaxation exhibited bulk water-like behavior. Increasing starch concentration reduced the amount of bulk water in the system and hence, the water molecules exhibiting the high frequency relaxation decreased.

The three states of water revealed by the dielectric spectra could be compared to the classic water binding regimes which propose multimolecular layering of water sorbed on starch. Based on the BET model (Brunauer, Emmett, & Teller, 1938), several studies have suggested the presence of a monolayer of water tightly bound to hydroxyl groups of starch chains (Hellman & Melvin, 1950; Timmermann, Chirife, & Iglesias, 2001; van den Berg, 1981). The monolayer moisture content of starch has been reported to be in the range of 0.079–0.098 g water/g dry starch (Choi & Kerr, 2003; Hellman & Melvin, 1950; Timmermann et al., 2001; van den Berg, 1981) which was close to the range of low frequency water observed in this study (0.081–0.161 g water/g dry starch).

According to the BET model, the secondary and higher layers of water have similar characteristics as liquid water (Hartley, Kamke, & Peemoeller, 1992). Dent (1977) modified the BET model to suggest that secondary and higher layers of water were thermodynamically similar to each other but different than bulk water. This notion was also supported by Guggenheim, Anderson and de Boer (GAB) sorption model (Timmermann et al., 2001). The relaxation time of the intermediate frequency process (20–25 ps) was almost ~4 times shorter than bulk water (4–9 ps). Hence, it could be postulated that water molecules exhibiting intermediate frequency relaxation were different than bulk water and similar to the secondary layer of moisture indicated by the GAB and Dent models. On the other hand, the water molecules exhibiting the high frequency relaxation had bulk water-like behavior and hence they could be compared to higher layers of moisture as proposed by the BET model. It is noteworthy that above-mentioned water sorption models (BET, GAB, Dent) describe moisture sorption behavior in a range of relative humidity environments. Though the starch–water systems used in this study had very high moisture contents as compared to moisture sorption in relative humidity environments, comparable amounts of monolayer and low frequency water indicate similarities in the moisture sorption behavior of monolayer water irrespective of the physical environment.

The relaxation time of low frequency water describes the nature of interaction between the monolayer water molecules and polymer chains. The low frequency water associated with starch exhibited shorter relaxation times as compared to that exhibited by several other biomaterials (0.9–2 ns) (Mashimo et al., 1987). On the other hand, monolayer water associated with 34% lysozyme solution had a relaxation time of 640 ps (Pethig, 1992). The slowest water population associated with hydrated Nafion membranes had a relaxation time range of 78–94 ps (Lu, 2005). The activation energy of the low frequency water is ~3.4–5.3 kJ/mol which is much lower than that of bulk water (15.9 kJ/mol) (Lu, 2005). The effective dipole moment of these low frequency highly confined water molecules is 0.79 Debye which is ~3 times lower than that for bulk water (2.5 Debye) (Pethig, 1992). Longer relaxation time of these highly confined water molecules implies increased rotational hindrance and decreased involvement with correlated orientations of surrounding water molecules and hydrogen bonds.

The relaxations due to the segmental motion of starch polymer chains are usually observed in a lower frequency range (10^{-3}–10^{6} Hz) (Majumder et al., 2004, 2006) as compared to the range used in this study (10^{8}–10^{10} Hz). Hence, it was quite unlikely that the three observed relaxations were due to motion or dipolar interactions of starch glucose units.

Similar distributions of different populations of water present in the starch–water system have been reported previously (Gonera & Cornillon, 2002; Le Botlan et al., 1998; Ritota, Gianferri, Bucci, & Brosio, 2008; Tang et al., 2000). Tang et al. (2000), using ^{1}H and ^{2}H NMR methods, reported two populations of water molecules associated with packed bed of maize starch granules at 17 °C. The population exhibiting slower dynamics (spin–spin relaxation time, $T_2 = 25$ ms) was assigned to extragranular bulk water. The faster relaxation ($T_2 = 3$ ms) was proposed to be due to two intragranular water populations – water in amorphous growth rings and water in amorphous regions in the semi-crystalline lamellae. The authors suggested that these two populations were in fast diffusional exchange with each other. Recently, Ritota et al. (2008) reported four populations of water molecules in 25% rich starch slurry based on the analysis of NMR relaxation curves. Using a diffusive and chemical exchange model, the four populations were assigned to extragranular water, water associated with the amorphous regions of the granule and water trapped in amylose or amylopectin helices in the crystalline regions. These previous studies also indicated that water molecules in various sub-populations inside or outside the granule were in dynamic exchange with each other. This could possibly explain the overlapping of various dielectric relaxation peaks observed in our study.

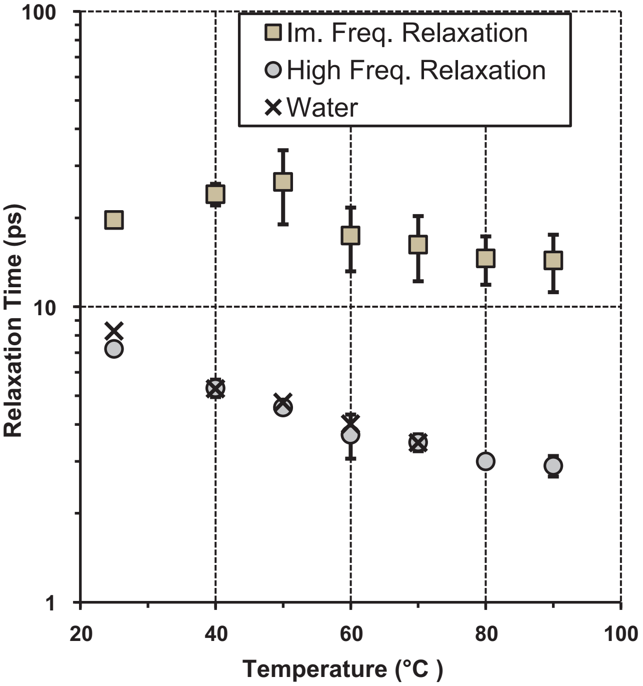

Fig. 5. Effect of heating on the high and intermediate frequency relaxation times of 10% starch slurry. Relaxation time of water as a function of temperature was obtained from Kaatze (1997) and Von Hippel (1988). Error bars represent one standard deviation above and below the mean value.

3.3. *Effect of heating on dielectric response*

The effect of heating on high and intermediate frequency relaxation times of 10% starch slurry is shown in Fig. 5. The τ_h values for 10% starch slurry decreased upon elevating the heating end temperature from 25 to 60 °C, but did not change significantly ($P > 0.18$) upon heating to higher temperatures. The drop in τ_h values upon heating has also been observed previously in dilute aqueous suspensions of various starches, gellan gum and albumin (Casasnovas, 2006; Mashimo et al., 1996; Miura et al., 1994). This drop in τ_h is expected since bulk water τ_h has an inverse relationship with temperature described by,

$$\tau_h = \frac{1}{T} e^{2140/T} \times 10^{-12}\ \text{s} \tag{7}$$

where T is the temperature in Kelvin (Sihvola, 1999). The τ_h values in 10% starch slurry were similar those of the relaxation times of bulk water reported in the literature (Kaatze, 1997; Von Hippel, 1988). No significant change in τ_h values upon heating to higher temperatures (>60 °C) suggested that structural changes occurring in the granules during gelatinization were also influencing the bulk water dynamics. This was further supported by Casasnovas (2006), who reported a change in slope of τ_h vs. temperature curve of dilute aqueous suspensions of potato and waxy maize starches during heating in the temperature range of 65–80 °C.

The intermediate frequency relaxation time (τ_{im}) of 10% starch slurry was not significantly influenced by heating ($P > 0.71$). Hence, gelatinization did not influence the rotational mobility of slower relaxing water species.

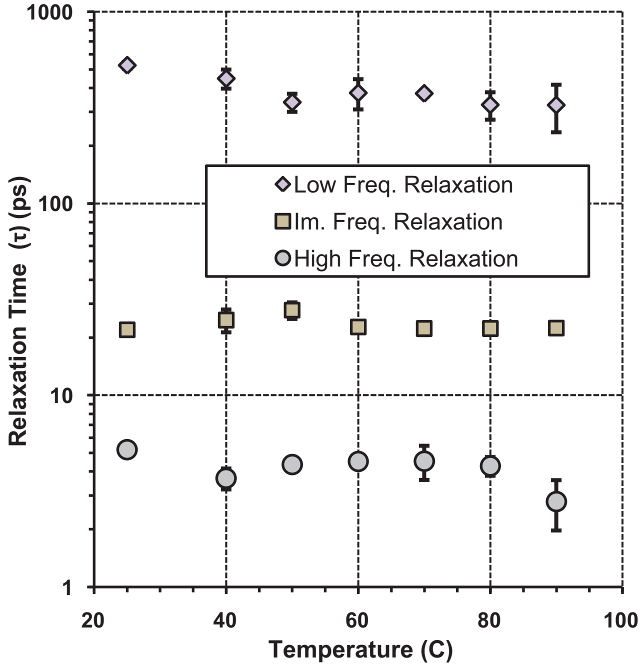

Fig. 6. Effect of heating on the high, intermediate and low frequency relaxation times of 50% starch slurry. Error bars represent one standard deviation above and below the mean value.

The τ_h, τ_{im} and τ_l values for 50% starch slurry did not change significantly upon heating ($P > 0.91$) (Fig. 6). Similarly, for 30% starch slurry, no significant differences ($P > 0.19$) were observed in the three relaxation times upon heating the slurries up to 90 °C (data not shown).

The mobility of high frequency relaxation (bulk water) increased progressively upon heating to 60 °C for 10% starch slurry, but was largely unaffected over the entire temperature range for 30% or 50% starch slurries. This suggested that heat energy being input was entirely being used for disruption of native granular structure, and the mobility of water was largely unaffected. Tang, Brun, and Hills (2001) also reported no shift in the NMR transverse relaxation peak associated with bulk water during gelatinization of water saturated bed of potato starch granules (45% starch). It was interesting to note that even at high starch concentrations (50% starch), where limited water was available for granule swelling, the high frequency relaxation did not disappear upon heating, even though no extragranular water is expected to be left after heating the slurries to higher end temperatures. This indicated that water present inside the poorly swollen starch granules could also exhibit bulk water like behavior. However, some studies, using NMR methods, have reported disappearance of the bulk water relaxation peak after gelatinization of starch–water systems containing up to 52% water (Ritota et al., 2008; Tananuwong & Reid, 2004). This discrepancy in NMR and dielectric relaxation results could be due to the different sensitivities and time scales of molecular motion being probed by these two methods.

Previous studies have also reported no significant changes in water mobility during starch gelatinization at starch concentrations comparable to this study. Ritota et al. (2008) reported that mobility of the most highly restrained water species in 25% rice starch slurry exhibited a flat trend during gelatinization. It is possible that the increase in kinetic energy upon elevation of temperature was not enough to bring about a change in the rotational mobility of the slowly relaxing molecules. Hence, their relaxation dynamics was not influenced by heating. Also, as indicated earlier, the heat energy input was possibly being used for the disruption of native granular structure, and hence water mobility was not influenced.

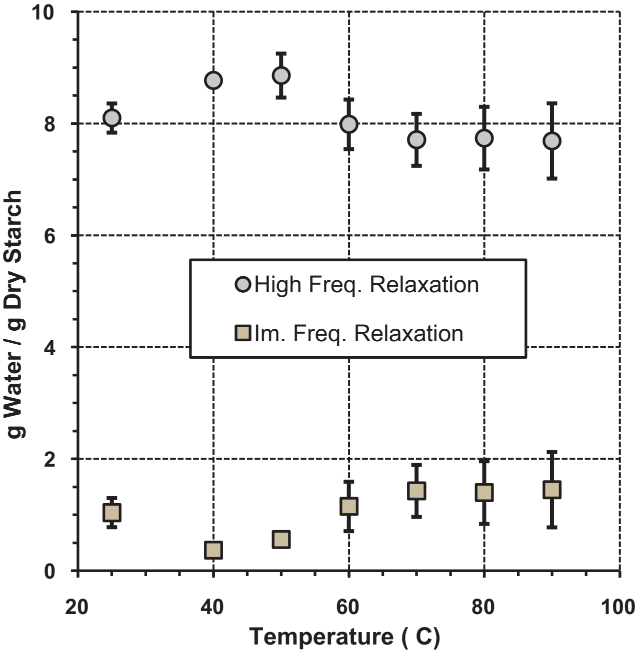

Fig. 7. Effect of heating on the amount of water exhibiting high and intermediate frequency relaxations observed in the dielectric response of 10% starch slurry. Error bars represent one standard deviation above and below the mean value.

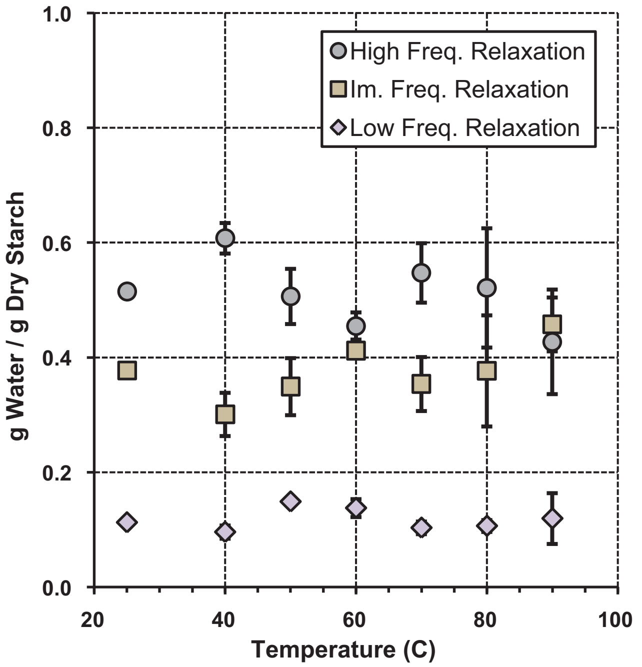

Fig. 8. Effect of heating on the amount of water exhibiting high, intermediate and low frequency relaxations observed in the dielectric response of 50% starch slurry. Error bars represent one standard deviation above and below the mean value.

The effect of heating on the amount of water associated with each relaxation observed in the dielectric spectra of 10% and 50% starch slurries is shown in Figs. 7 and 8, respectively. The high frequency relaxation was the most dominant relaxation while the low frequency relaxation was the weakest relaxation at all temperatures for the starch concentrations examined in the study. In the temperature range of 25–90 °C, the amount of bulk water (i.e.

water exhibiting high frequency relaxation) was between 7.8 and 8.9 g water/g dry starch for 10% starch slurry, 1.4–1.8 g water/g dry starch for 30% starch slurry (data not shown) and 0.4–0.6 g water/g dry starch for 50% starch slurry. For the sake of comparison, the amount of bulk water in 25% rice starch slurry, in the temperature range of 20–54 °C, was between 0.5 and 1.6 g water/g dry starch when calculated on the basis of NMR T_2 measurements, and between 1.2 and 2.1 g water/g dry starch when calculated using NMR T_1 measurements (Ritota et al., 2008). For 45% potato starch slurry, the proportion of extragranular water, measured using NMR T_1 measurements was ~0.9 g water/g dry starch at 25 °C (Tang et al., 2000).

Heating did not have any significant effect ($P > 0.187$) on the relative strengths of high, intermediate and low frequency relaxations at all of the starch concentrations. This indicated that gelatinization did not influence the relative distribution of water in the three water species. Water absorption during swelling of granules reduces the amount of extragranular water. However, the results indicated that the majority of water molecules in starch–water system exhibited bulk water like behavior even though there was no extragranular water left after heating starch slurries to higher temperatures. Mashimo et al. (1996) also reported that majority of the water present in the gellan gum gel exhibited bulk water-like dynamics. This was attributed to formation of clusters of bulk water molecules enclosed by the bound water molecules inside the gel matrix.

Dielectric spectroscopy data of starch–water systems suggest that relaxation time can be used for monitoring the mobility of water during processing of starch-based foods. Also, relaxation strength can be used to monitor relative concentration of starch and water during food processing. However, little or no change in relaxation parameters in the gelatinization temperature range indicates that change in water mobility is not a strong indicator of the degree of starch gelatinization.

4. Conclusions

This study showed that aqueous starch systems have up to three species of water molecules with different rotational mobilities. The rotational mobility of the two slower relaxing water species is not significantly influenced ($P > 0.712$) by gelatinization at all starch concentrations. The rotational mobility of bulk water, which is the most mobile water species, is reduced upon gelatinization at low starch concentration (10% starch), but remains unaffected at higher starch concentrations. The relative water distribution in the three water species is not significantly influenced ($P > 0.187$) by gelatinization and majority of water molecules exhibit bulk water like behavior even though there is no extragranular water left due to water absorption during granular swelling. Using the Kirkwood model, the amount of water exhibiting the slowest relaxation (230–620 ps) was calculated to be 0.08–0.16 g water/g starch, which is close to the literature values of monolayer water associated with wheat starch. Even after the loss of majority of the double helical order and disruption of native granular structure, the three relaxation peaks do not merge or disappear. This indicates that native granular order is not necessary for the existence of the three water species.

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