Gelatinization of Wheat Starch in the Presence of Sucrose and Sodium Chloride: Correlation Between Gelatinization Temperature and Water Mobility as Determined by Oxygen-17 Nuclear Magnetic Resonance

PAVINEE CHINACHOTI, MAL-SHICK KIM-SHIN, FRANK MARI, and LEAH LO

ABSTRACT

The inhibitory effect of sucrose and NaCl on starch gelatinization was investigated by differential scanning calorimetry and nuclear magnetic resonance (NMR) spectroscopy. The increase in gelatinization temperature ($T_g$) resulting from added solutes was correlated to various physical properties, such as water activity, solute-solvent average molecular weight, and $^{17}$O NMR $D_2O$ mobility. As the solute concentration increased, $^{17}$O relaxation time ($T_2$) decreased, indicating that $D_2O$ mobility decreased. This reduced the plasticizing effect, leading to an increased $T_g$. However, the dependency of $T_g$ on $D_2O$ mobility was limited to only some solute concentrations. At a sucrose concentration above 20% (w/w), $T_g$ increased with solute content, but $T_g$ remained relatively constant, resulting in a negative correlation. A decrease in free volume by added solutes also played an important role. A balance between both of these factors was proposed to be responsible for the final $T_g$. The $T_g$-$T_s$ relationship for NaCl was complicated by ionic properties, which resulted in a much higher $T_g$ at a given $T_s$ than for sucrose, regardless of its smaller molecular weight.

Studies have proposed that sugars increase the gelatinization temperature ($T_g$) of starches by various means, such as their ability to compete for water against starch and reduce the system water activity ($a_w$) (D’Appolonia 1972, Derby et al 1975, Labuza 1975), the sugar-starch interaction (Lelièvre 1976; Spies and Hoseney 1982; Hansen et al 1987, 1989), and the increase in free volume, resulting in less plasticizing effect of the sucrose-water solvent (Levine and Slade 1988, 1989). The effects of salt have also been studied and are reportedly quite different in mechanism, since salts may affect the physical property of the water (J. Jane, personal communication, 1990) and Donnan potential due to cation-starch interactions (Oosten 1982, 1983).

Nuclear magnetic resonance (NMR) spectroscopy is one of the best alternatives for determining the molecular dynamics of starch, as reviewed by Chinachoti et al (1991). NMR shows that water mobility, as measured by relaxation time ($T_2$), decreases drastically during starch gelatinization. In the presence of solutes, such as sugar and salt, $T_2$ for water was lowered and has been hypothesized to play an important role in the antiplasticizing effect on starch (Chinachoti et al 1991). As Levine and Slade (1988, 1989) pointed out, using the $a_w$ concept to try to explain the phenomenon above is inappropriate, because $a_w$ cannot provide direct information regarding the molecular dynamics and thus the plasticizing property of the water. Levine and Slade also mentioned that this plasticizing property was rather dependent on translational mobility, which could be approximated by rotational mobility of a solute-solvent system. Unfortunately, little has been reported to correlate the mobility of water to its ability to gelatinize starch.

Despite the increasing number of $^{17}$O NMR (O-NMR) experiments to determine water mobility, little has been reported on starch gelatinization at elevated temperatures. An earlier paper (Chinachoti et al 1991) showed the versatility of such techniques for understanding the dynamic molecular changes during gelatinization. Because of their common use in foods, sucrose and NaCl were selected for this work. Our objective was to use the measurement of O-NMR mobility to study the inhibitory effects of sucrose and NaCl on starch gelatinization and to relate these effects to changes in $a_w$, free volume, and mobility.

MATERIALS AND METHODS

Wheat starch (Manildra Milling Corp, Minneapolis, MN), deuterium oxide (99%, Wilmad Glass Co., Inc., Buena, NJ), sucrose, NaCl, glucose, and fructose (Fisher Scientific Co., Fairlawn, NJ), were used. All samples contained starch and free water ($D_2O$)(40:60). Sucrose, NaCl, fructose, or glucose was added to starch to make a given mixture of starch, solute, and $D_2O$. The sucrose content (starch basis) ranged from 0 to 41.3%, NaCl (starch basis) from 0 to 30%; glucose and fructose were both 10%. The samples were mixed mechanically and left resting overnight before the gelatinization experiment. $D_2O$ instead of $H_2O$ was used to avoid the proton exchange broadening of the $^{17}$O water peak (Richardson et al 1987).

Differential Scanning Calorimetry

A differential scanning calorimeter (DSC2, Perkin Elmer Corp., Norwalk, CT) was used to measure $T_g$. A 10-mg starch sample was weighed and sealed in a hermetically sealed pan and then heated under the DSC from 7 to 160°C at a rate of 10°C/min. An empty pan was used as the reference. The initial temperature ($T_0$) and peak temperature ($T_p$) were measured by thermal analysis data system (Lund 1983).

NMR

A starch sample was heated in the NMR probe from 25 to 45°C in a 10-mm NMR tube (Wilmad Glass Co., Inc., Buena, NJ). After reaching 45°C, an O-NMR spectrum was obtained. $^{17}$O in natural abundance ($3.7 \times 10^{-2}$%) was used. The spectra were obtained at 40.67 MHz with a Varian XL-300 instrument. Spectra width was 20,000 Hz; pulse width, 15 μsec; recycle delay, 15 msec; number of scans, 6,000. A set of duplicate samples was tested. The experimental error was within 5% (the average is used here). The transverse relaxation rate ($R_2$) was calculated from the line width ($Δν$) at half height of the Fourier transformed spectra as $R_2 = πΔν$.

RESULTS AND DISCUSSION

DSC Results

The DSC data for the water-mediated gelatinization process (the 60°C peak) are shown in Table I for starch-$D_2O$ mixtures (40:60) with various solutes. As expected, where sucrose and NaCl were present, $T_g$ and $T_s$ increased as the solute content increased. The $T_g$ of the wheat starch increased as more solutes were added (Fig. 1); the increase in $T_g$ caused by NaCl was greater than the increase caused by sucrose of the same concentration. At the 10% sugar level, no significant differences were observed in $T_g$ among the samples containing sucrose, glucose, and fructose.
A number of explanations have been proposed for the antiplasticizing effect of these solutes. The classic explanation is competition for water among the solids, resulting in a lowered \( a_w \); thus less water is available for the gelatinization process.

**TABLE I**

Results of Differential Scanning Calorimetry for the Endothermic Gelatinization of Wheat Starch in Free Water* in the Presence of Sucrose, Sodium Chloride, Glucose, and Fructose

<table>
<thead>
<tr>
<th>Additive</th>
<th>Percent (starch basis)</th>
<th>Temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>60.93 ± 0.33</td>
<td>66.15 ± 0.38</td>
</tr>
<tr>
<td>Sucrose</td>
<td>10.0</td>
<td>63.01 ± 0.63</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>64.67 ± 0.09</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>65.67 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>41.3</td>
<td>67.48 ± 0.14</td>
</tr>
<tr>
<td>Glucose</td>
<td>10.0</td>
<td>62.69 ± 0.60</td>
</tr>
<tr>
<td>Fructose</td>
<td>10.0</td>
<td>63.21 ± 0.09</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.5</td>
<td>62.29 ± 0.16</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>64.82 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>66.14 ± 0.88</td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td>65.96 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>67.39 ± 0.37</td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>67.36 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>10.0</td>
<td>70.08</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>70.21</td>
</tr>
<tr>
<td></td>
<td>30.0</td>
<td>68.77</td>
</tr>
</tbody>
</table>

*Ratio of wheat starch to free water = 40:60; scanning rate = 10°C/min.

Fig. 1. Gelatinization temperature for wheat starch in the presence of free water (60:40), sucrose (Δ), and NaCl (□) at various concentrations. Gelatinization temperature in the presence of 10% (starch basis) sucrose (▲), fructose (▼), and glucose (●).

Fig. 2. Gelatinization temperature plotted against water activity, calculated from mixtures of starch and free water (40:60) with various levels and types of solutes. □ = NaCl, ▲ = sucrose, ▼ = fructose, ● = glucose.

(D'Appolonia 1972, Derby et al. 1975, Labuza 1975). To facilitate this argument, \( a_w \) for each sample (25°C) was calculated based on a mass balance (Chinachoti 1990) and plotted against \( T_g \) (Fig. 2). Although some correlation was observed between \( a_w \) and the plasticizing properties, \( a_w \) is not appropriate to describe the plasticizing properties of the water (Levine and Slade 1988, 1989). Levine and Slade (1989) suggested that the antiplasticizing properties of these sugars are rather related to the decreased free volume of the liquid fraction (sugar-water cosolvent), which can be represented by the increasing average molecular weight (mol wt) of the liquid fraction. As a result, the free volume of the amorphous fringes in the fringe micelle of starch granules has less ability to increase due to a decrease in chain mobility (Levine and Slade 1989). These authors also showed that a plot between \( T_g \) and the inverse of the of the mol wt was linearly correlated in sugars of 50% aqueous concentration.

Our results were plotted in a similar fashion (Fig. 3) but show a curvilinear relationship, which could be explained by the fact that our samples varied in the aqueous concentration of sugar, ranging from 0 to 27%. The type of solutes was important to this relationship; sucrose, glucose, and fructose were similar, whereas NaCl showed a much higher increase in \( T_g \) at a given average mol wt (Fig. 3). NaCl, added only at 0–3% (starch basis), increased sharply in \( T_g \) (Fig. 3, I). \( T_g \) then leveled off at 10–20% NaCl (Fig. 3, II). As indicated previously (Oosten 1982, 1983; Chungcharoen and Lund 1987; Chinachoti et al. 1991), ionic inter-

Fig. 3. Gelatinization temperature of wheat starch in free water (40:60) in the presence of sucrose (Δ) and NaCl (□) as a function of the inverse of the average molecular weight (Mw) of the solute-D2O cosolvent. Data in the presence of and fructose (▼) and glucose (●).

Fig. 4. Changes in \( ^{17}O \) NMR relaxation time \( (T_2) \) for free water in wheat starch (60:40), measured at 45°C in the presence of varying concentrations of sucrose (Δ), NaCl (□), fructose (▼), and glucose (●).

246 CEREAL CHEMISTRY
actions between cations (sodium, in this case) played an important role in the gelatinization process. It has been proposed that the resulting increased Donnan potential excludes the anions from the starch granules. This interaction is probably limited and dependent on the concentration and ionic strength of the solute.

**NMR Results**

The relationship between \( T_p \) and \( a_w \) and between \( T_p \) and the average mol wt of cosolvents has been demonstrated above. This section presents the relationship between \( T_p \) and \( D_2O \) mobility as determined by O-NMR. Figure 4 shows the O-NMR \( T_2 \) representing the \( D_2O \) mobility just before the gelatinization process. As plotted against solid content or the amount of added solutes (Fig. 4), \( T_2 \) decreased rapidly at the beginning and then leveled off. The decreased \( T_2 \) indicated a significant decrease in the \( D_2O \) mobility in the presence of sucrose and NaCl (at a given \( D_2O \) content). At some higher levels of sucrose and NaCl, \( T_2 \) decreased less drastically and appeared to approach some asymptotic levels. \( T_p \) was much more sensitive to NaCl than to sucrose. This corresponds with the finding that \( T_p \) was also more sensitive to NaCl than to sucrose of the same concentration, which could be related to the decreased \( T_p \) (i.e., decreased \( D_2O \) mobility).

When \( T_p \) was plotted against \( T_2 \) (Fig. 5) from the O-NMR scans, \( T_p \) increased in a curvilinear fashion as \( T_2 \) decreased (i.e., \( D_2O \) mobility decreased due to the added solute). For sucrose, \( T_p \) increased with the decreased \( T_2 \) only moderately at first; as the sucrose level increased beyond 10% (starch basis), \( T_p \) increased more abruptly, whereas \( T_2 \) remained relatively unchanged (Fig. 5, \( T_2 \) from 1.2 to 1.6 \( \times 10^{-3} \) sec). At the same 10% concentration, adding glucose or fructose did not affect \( T_p \) any differently than did adding sucrose, though it decreased the \( D_2O \) mobility to a greater extent than did sucrose (Fig. 5). This indicates that \( D_2O \) mobility was not the only factor involved. Because glucose and fructose have a lower mol wt than does sucrose, they could have contributed to a greater degree of plasticization than sucrose of the same concentration. This is probably why \( T_p \) for such samples was quite low, considering that their \( D_2O \) mobility is lower than that of sucrose, and thus should result in a higher \( T_p \).

For NaCl (Fig. 5), \( T_p \) drastically increased with decreasing \( T_2 \) on addition of a low level of NaCl (1–2%). As the NaCl concentration further increased, no significant change in \( T_p \) was found until the 10% level of NaCl, when \( T_p \) again rose sharply. This resulted in an S-shaped curve. For a given \( T_2 \), \( T_p \) for a sample containing NaCl was always higher than that for a sample containing sucrose. Except for the first point (starch alone) on the NaCl curve in Fig. 5, the overall curve for the \( T_p-T_2 \) relationship was very similar to that of sucrose, i.e., the two curves were almost parallel. This could mean that the ionic interaction between NaCl and starch raised \( T_p \) to a higher level at a low (1–2%) concentration; the \( T_0^* - T_2 \) relationship at NaCl levels higher than this fell in the same pattern as that for sucrose. Thus, the ionic property of NaCl played an important role. This contribution of the ionic interaction between sodium and the hydroxyl groups of starch polymers has been pointed out by various investigators (Oosten 1982, 1983; Chungcharoen and Lund 1987). Recent work on NMR (Chinachoti et al. 1991) showed Na-starch interactions, as indicated by a line broadening of \( \gamma^2 \)Na spectra during starch gelatinization.

**CONCLUSION**

The present work presents different views of analysis and interpretation of the inhibitory effect of sucrose and NaCl on starch gelatinization. Although the increased solute concentration also resulted in a lower \( a_w \), the increase in \( T_p \) is better explained in terms of other physical properties, i.e., the average mol wt of the cosolvent (Levine and Slade 1988) as well as the molecular mobility of the solvent. The O-NMR transverse \( T_2 \) increased with added solutes, indicating a decrease in \( D_2O \) mobility. For the base of sugars, replacing sucrose with glucose or fructose did not change the \( T_p \) despite the decreased \( T_2 \). This was probably due to the reduced average mol wt of the cosolvent for glucose or fructose. The effect of NaCl showed that the \( T_p-T_2 \) relationship was complicated by some contribution of the ionic interaction in a 1–2% NaCl concentration, which resulted in a much higher \( T_p \) at a given \( T_2 \) than for sucrose. The \( T_p-T_2 \) relationship at higher NaCl concentrations paralleled that for sucrose. Solvent mobility was useful for expressing starch gelatinization.

**ACKNOWLEDGMENTS**

We acknowledge the University High Field NMR facility and the Polymer Science Department for access to the Varian XL-300 NMR spectrometer and the differential scanning calorimeter, respectively.

**LITERATURE CITED**


OOSTEN, B. J. 1982. Tentative hypothesis to explain how electrolytes affect the gelatinization temperature of starches in water. Starch/

Mobility of water in corn starch suspensions determined by nuclear magnetic resonance. Starch/Stärke 39:79.

[Received May 2, 1990. Accepted November 9, 1990.]