Influence of Solutes and Water on Rice Starch Gelatinization

A. CHUNGCHAROEN and D. B. LUND

ABSTRACT

Gelatinization phenomena in rice flours and isolated starches from the Lemont variety and a mixture of Nato and Mars varieties were investigated using differential scanning calorimetry. When a flour or starch suspension in an excess amount of water was heated to 130°C at 10°C/min, gelatinization endotherm was observed at a temperature range of 65–86°C. No difference was found between the gelatinization characteristics of flours and their isolated starch counterparts. In the presence of sucrose or sodium chloride, gelatinization temperatures shifted to higher temperatures, and enthalpy associated with the endothermic process decreased. The extent of temperature shift and enthalpy change was dependent on the water-to-starch ratio. Influence of sucrose on gelatinization temperature could be explained by considering starch as a partially crystalline glassy polymer. A surfactant containing 90% glyceryl monooleate had a slight effect on gelatinization temperature and had no effect on enthalpy of the endothermic process.

The influence of ionic and nonionic solutes on starch gelatinization has been studied by many investigators, and it is well known that gelatinization characteristics are markedly altered by the addition of certain chemicals. Some salts accelerate the disruption of hydrogen bonds to assist gelatinization as reported by Leach (1965) and Lindqvist (1979), whereas others inhibit gelatinization by acting as salting-out agents (Ganz 1965, Lindqvist 1979). Sugars are also known to retard gelatinization by inhibiting swelling of starch granules in a water system (D’Appolonia 1972, Bean and Yamazaki 1978, Savage and Osman 1978, Wootten and Bamunuarachchi 1980). Certain lipids form complexes with amylose and change the starch gelatinization characteristics (Collison and Elton 1961, Osman et al 1961, Ito et al 1970, Ghiassi et al 1982). Because most of these studies were on starch sources other than rice, we are reporting gelatinization characteristics of rice flour and isolated starch in the presence and absence of sugar, salt, and surfactant.

MATERIALS AND METHODS

Materials

Milled rice samples of the long-grain Lemont variety and from a physical mixture of Nato and Mars varieties (medium grain length) were used. All rice samples were ground using an analytical Wiley mill and sieved through a 100-mesh sieve. Rice starches were isolated from the flours by dilute sodium hydroxide extraction using the method of Al-Bayati and Lorenz (1975).

Amylose contents, as determined by amperometric titration using the method described by BeMiller (1964), of the rice samples from the Lemont variety were 23.7% (dry basis) for the flour and 25.9% (dry basis) for the starch, whereas the amylose contents of the rice samples from a mixture of Nato and Mars varieties were 16.6 and 18.4% (dry basis) for the flour and starch, respectively.

The sucrose was commercial, fine granulated food grade. Sucrose-to-starch or sucrose-to-flour ratio was held constant at 0.4:1. The sucrose concentrations in the aqueous phase were 3.9, 28.6, and 47.1% (w/w) for samples with water-to-starch ratios of 10:1, 1:1, or 0.45:1, respectively. The salt was reagent grade sodium chloride crystals. Salt-to-starch or salt-to-flour ratio was held constant at 0.04:1. Sodium chloride concentrations in the aqueous phase were 0.4, 3.9, and 8.2% (w/w) for samples with water-to-starch ratios of 10:1, 1:1, or 0.45:1, respectively. The surfactant was commercial food grade surfactant, Myvaplex 600, which contained at least 90% glyceryl monooleate (Eastman Chemical Products, Inc., Kingsport, TN). Surfactant-to-starch or surfactant-to-flour ratio was held constant at 0.004:1. Surfactant concentrations in the aqueous phase were 0.04, 0.4, and 0.9% (w/w) for samples with water-to-starch ratios of 10:1, 1:1, and 0.45:1, respectively.

Methods

A DuPont model 990 thermal analyzer with a differential scanning calorimeter cell was used to measure gelatinization temperatures and enthalpy. Samples for thermal analysis were prepared by weighing the required amount of starch (or flour) and solution and mixing to a uniform paste. The wetted samples were allowed to equilibrate for at least 1 hr before differential scanning calorimetry (DSC) analysis. Approximately 15 mg of sample was weighed into coated aluminum calorimeter pans (DuPont) and hermetically sealed using a sample-encapsulating press. A sample pan containing a weight of distilled water equal to that of the sample (about 15 mg) was used as a reference. The samples were heated from 10 to 130°C at 10°C/min in the calorimeter. The calorimeter was calibrated using indium metal. The influence of scanning rate on the DSC endotherm was assessed by subjecting samples of 10:1 water-to-rice starch ratio to various heating rates. The peak gelatinization temperatures were approximately 2°C higher at a heating rate of 10°C/min compared to the peak gelatinization temperature extrapolated to 0°C/min heating rate. Because the objective of the study was to compare the influence of solutes and moisture on gelatinization characteristics of rice starch and flour, all data are reported at a heating rate of 10°C/min.

A polarizing microscope with mounted camera was used to examine changes in the starch granules during gelatinization. Rice flour and starch samples were heated in the calorimeter at 10°C/min from ambient temperature to a termination temperature corresponding to the onset, peak, or conclusion temperature for each sample, respectively. After cooling, the pan was punctured, and a sample was withdrawn and carefully dispersed in water. A drop of this suspension was examined under polarized light.

RESULTS AND DISCUSSION

Effect of Sucrose

A typical endotherm obtained from DSC when rice flour or starch suspension was heated in the presence of sucrose is given in Figure 1. Gelatinization temperatures and enthalpy are given in Tables I and III, respectively, for rice flour and in Tables II and IV, respectively, for rice starch. For all samples, gelatinization temperature increased and enthalpy decreased when sucrose was added to the system. The increase in gelatinization temperature and decrease in enthalpy were even more pronounced in limited-water systems than in excess-water systems. The results were qualitatively similar in both varieties of rice even though they differed in amylose content. Observations of starch granules under

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polarized light showed a delay in loss of birefringence when sugar was present, thus confirming the results found by DSC.

Wada and co-workers (1979) studied gelatinization of potato starch using differential thermal analysis and found that initial gelatinization temperature was higher in 30 to 50% sucrose solution than in the absence of sugar. Their finding agrees very well with the results presented in this report. Using DSC, Wootten and Bamunuarachchi (1980) reported an increase in the peak temperature of gelatinization of wheat starch, but they found no effect of sugar on the initial or conclusion temperature. Ghiasi et al. (1983) also observed an increase in gelatinization temperature of wheat starch as sucrose concentration increased. Savage and Osman (1978) found that sugar inhibited swelling of corn starch in water and retarded gelatinization. Bean and Yamazaki (1978) reported an increase in temperature of birefringence disappearance of wheat starch when sugar was present. The application of sucrose-gelatinization temperature interaction was suggested by Bean et al. (1983). When substituting rice flour for wheat flour in cake baking, they found that to obtain desirable layer-cake quality, optimum water absorption was 20% lower for rice flour than for wheat flour. When water was decreased substantially in the cake formulation, it was necessary to adjust the amount of sugar used in the formula so that starch gelatinization and granule swelling would occur concurrently with maximum batter expansion to get cakes with required volumes and contours. Spies and Hoseney (1982) suggested that other properties of sugar, in addition to water-binding capacity, affected gelatinization. They explained that sugar or any small solute when added to water decreased the water activity of the system. Thus, the ability of water to interact with other components in the system decreased, resulting in higher energy requirements.

Recently, however, Maurice et al. (1985) and Biladeris et al. (1986) suggested that ungelatinized starch can be considered a partially crystalline glassy polymer and that gelatinization is the nonequilibrium melting process that occurs upon the application of heat. There is a glass transition of the amorphous regions that occurs at a lower temperature than the true melting process of the crystalline regions. The glass transition must precede melting and is influenced by materials that serve as plasticizers. Water is a plasticizer for starch, and as moisture content increases from about 10 to 30%, the glass transition temperature decreases. This was observed by Wirarikataksunah (1980) for rice starch. When a solute such as sucrose is added to water, the solution is a less effective plasticizer because the weight-average molecular weight is greater than that for water alone. Our observations confirm this explanation, because the onset temperature of the overall endothermic process increased as moisture concentration

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![Diagram of endothermic heat flow](source)

**Fig. 1.** Endotherms of rice starch suspensions heated from 30 to 130°C at 10°C/min and water-to-solid ratios of 10:1 with no sucrose (a) or with sucrose (b); 1:1 with no sucrose (c) or with sucrose (d); and 0.45:1 with no sucrose (e) or with sucrose (f), respectively.

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### TABLE I

<table>
<thead>
<tr>
<th>Rice Variety</th>
<th>Water/Flour Ratio</th>
<th>Onset (°C)</th>
<th>With Solute</th>
<th>No Solute</th>
<th>Sucrose</th>
<th>NaCl</th>
<th>Surfactantb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nato and Mars</td>
<td>10:1</td>
<td>66.5</td>
<td>68.0</td>
<td>68.0</td>
<td>73.6</td>
<td>75.0</td>
<td>76.0</td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>66.5</td>
<td>68.0</td>
<td>76.0</td>
<td>76.8</td>
<td>89.3</td>
<td>86.0</td>
</tr>
<tr>
<td></td>
<td>0.45:1</td>
<td>69.0</td>
<td>92.6</td>
<td>90.0</td>
<td>83.3</td>
<td>111.6</td>
<td>106.3</td>
</tr>
</tbody>
</table>

| Lemont       | 10:1             | 74.3       | 76.0        | 76.0      | 78.9    | 81.0 | 81.5        |
|              | 1:1              | 74.5       | 84.0        | 82.0      | 81.5    | 93.0 | 90.0        |
|              | 0.45:1           | 77.0       | 98.0        | 96.0      | 85.3    | 115.6| 112.0       |

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### TABLE II

<table>
<thead>
<tr>
<th>Rice Variety</th>
<th>Water/Starch Ratio</th>
<th>Onset (°C)</th>
<th>With Solute</th>
<th>No Solute</th>
<th>Sucrose</th>
<th>NaCl</th>
<th>Surfactantb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nato and Mars</td>
<td>10:1</td>
<td>65.6</td>
<td>67.5</td>
<td>67.0</td>
<td>73.2</td>
<td>74.3</td>
<td>74.8</td>
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<tr>
<td></td>
<td>1:1</td>
<td>65.6</td>
<td>76.0</td>
<td>74.0</td>
<td>77.0</td>
<td>89.0</td>
<td>85.0</td>
</tr>
<tr>
<td></td>
<td>0.45:1</td>
<td>68.5</td>
<td>90.6</td>
<td>88.8</td>
<td>81.0</td>
<td>109.5</td>
<td>105.0</td>
</tr>
</tbody>
</table>

| Lemont       | 10:1              | 73.6       | 76.0        | 76.0      | 78.3    | 80.8 | 81.0        |
|              | 1:1               | 73.7       | 82.5        | 80.5      | 82.5    | 91.0 | 88.5        |
|              | 0.45:1            | 76.3       | 96.6        | 94.0      | 84.0    | 113.5| 110.6       |

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Three replicates. Standard deviation ± 0.5. Sucrose/flour ratio of 0.4:1; NaCl/flour ratio of 0.04:1; and surfactant/flour ratio of 0.004:1.

Meyvaplex 600, a commercial surfactant containing at least 90% gyceryl monostearate.
decreased and sucrose concentration increased. The observations reported in this study support the hypothesis of Biladeris et al. (1986) that granular starch consists of three phases—starch crystallites, a bulk amorphous phase consisting mainly of amylose, and intracrystalline amorphous regions consisting of dense branches of amylopectin. In this model, a decrease in moisture content results in an increase in the glass transition temperature of the bulk amorphous phase resulting in an increase in the temperature of the overall endothermic process of gelatinization. When solutes such as sucrose are added to the aqueous phase, less water is available to act as a plasticizer, and consequently the temperatures associated with gelatinization increase. Biladeris and co-workers (1986) concluded that for their rice samples the minimum requirement for water to fully exert its plasticizing effect on the granules is 30% (w/w). However, water also affects the melting temperature of the crystallites, an effect that is initiated at a glass transition temperature that is dependent on the moisture content. Therefore, at moisture contents between 70 and 30%, water has a compounding effect on gelatinization by influencing the glass transition temperature as well as the true melting temperature. In our studies with sucrose, the moisture content of rice starch samples ranged from 24% (w/w) (0.45:1.0.4 solution of water, starch, and sucrose) to 88% (10.1.0.4, water, starch, and sucrose), and we compounded the effect of sucrose with the effect of moisture.

**Effect of Sodium Chloride**

Sodium chloride was found to increase gelatinization temperature and decrease enthalpy of transition in all rice flour and isolated starch samples (Tables I–IV). Qualitatively, both rice samples behaved similarly. These results are similar to previous observations made by other investigators. At low concentrations, sodium chloride retarded gelatinization as found by Ganz (1965) and D’Appolonia (1972). Extended studies, however, show that as the concentration of sodium chloride increases, gelatinization temperature increases to a maximum and then decreases as concentration increases further (Oosten 1979, Evans and Haisman 1982). Wootton and Bamunuarachchi (1980) suggested that gelatinization temperature reaches a maximum at a concentration of 9% sodium chloride. They also explained that the decrease in enthalpy when salt was added to the system could arise from the influence of sodium and chloride ions on water, starch, and their interactions. When we examined our samples under polarized light, loss of birefringence was delayed as a result of addition of sodium chloride.

According to Oosten (1982), when sodium chloride was added to a starch or flour suspension, some alcohohic groups in the starch granules were converted to sodium alcoholates groups. These compounds were better dissociated, thus causing a rise in the Donnan potential, which more effectively excluded the chloride ions from the granules. However, the absorption of sodium ions was rather limited; hence, the increase in gelatinization temperature was also limited. Consequently, once gelatinization began (at a higher temperature), chloride ions assisted gelatinization by breaking hydrogen bonds between starch chains.

**Effect of Surfactant**

The effects of surfactant on gelatinization temperature and enthalpy are shown in Tables I–IV. In the excess-water system (10:1 water/flour or starch), surfactant at the concentration used in this study (surfactant/starch ratio of 0.004:1) increased gelatinization temperature. In the limited-water systems, there was an increase in gelatinization temperature in excess of that observed by simply reducing the water to starch or flour ratio. For example, from Table II, at a 0.45:1 water-to-starch ratio, the endotherm onset temperature was 68.5°C without surfactant (or salt or sugar) and 73.3°C with surfactant. Qualitatively, the effect of surfactant was similar for both rice varieties. The observation of an increase in temperature of the endothermic process with surfactant agrees with results of Larsson (1980). He reported a delay in the loss of birefringence of potato starch heated with 1% (w/w) monolaurin. Enthalpy of gelatinization was not affected by the presence of surfactant. Eliasson and co-workers (1981) also found no influence of the presence of lipid coating on enthalpy of potato starch when the starch was coated with monoglyceride so that the lipid content of the samples reached 0.7, 1.4, and 2.8% (w/w). Cloke et al (1983) found no difference in enthalpy for gelatinization of model cake systems with or without emulsifiers.

The ability to form a complex between a fatty adjunct and amylose has been well established, and this complex is known to affect physical characteristics of starch (Ghissi et al., 1982; Larsson 1980). In these studies, addition of surface-active agents to the system resulted in a marked increase in gelatinization temperature. This was explained by proposing that fatty adjuncts form a complex with amylose and repress swelling and solubilization. The fatty compound was involved in the helical configuration with amylose and formed a persistent outer layer to restrict passage of water into the starch granule and thus decreased swelling (Eliasson 1985). Furthermore, Biladeris et al. (1986) pointed out that whether the lipid-amylose complexes form without heating or only during heating is still unresolved. We observed that surfactants suppress gelatinization when water is limited in the system, and this could be explained by the hypothesis that lipid-amylose complexes can form at lower temperatures and influence gelatinization temperature.

### TABLE III

<table>
<thead>
<tr>
<th>Rice Variety</th>
<th>Water/Flour Ratio</th>
<th>No Solute</th>
<th>With Solute</th>
<th>Enthalpy (cal/g)</th>
<th>NaCl</th>
<th>Surfactantb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nato and Mars</td>
<td>10:1</td>
<td>2.04</td>
<td>1.95</td>
<td>1.99</td>
<td>2.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>1.86</td>
<td>1.44</td>
<td>1.50</td>
<td>1.80</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.45:1</td>
<td>1.45</td>
<td>1.08</td>
<td>1.18</td>
<td>1.38</td>
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<tr>
<td>Lemont</td>
<td>10:1</td>
<td>2.04</td>
<td>1.95</td>
<td>1.93</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1:1</td>
<td>1.88</td>
<td>1.46</td>
<td>1.55</td>
<td>1.82</td>
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<td>1.46</td>
<td>1.10</td>
<td>1.14</td>
<td>1.40</td>
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</table>

* Three replicates. Standard deviation ± 0.05. Sucrose/flour ratio of 0.41; NaCl/flour ratio of 0.041; and surfactant/flour ratio of 0.0041.
* Myvaplex 600, a commercial surfactant containing at least 90% glyceryl monostearate.

### TABLE IV

<table>
<thead>
<tr>
<th>Rice Variety</th>
<th>Water/Starch Ratio</th>
<th>No Solute</th>
<th>With Solute</th>
<th>Enthalpy (cal/g)</th>
<th>NaCl</th>
<th>Surfactantb</th>
</tr>
</thead>
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<tr>
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<td>3.12</td>
<td>2.86</td>
<td>2.89</td>
<td>2.96</td>
<td></td>
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<tr>
<td></td>
<td>1:1</td>
<td>2.88</td>
<td>2.06</td>
<td>2.12</td>
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<tr>
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<td>0.45:1</td>
<td>1.84</td>
<td>1.57</td>
<td>1.63</td>
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<tr>
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<td>3.12</td>
<td>2.85</td>
<td>2.90</td>
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<tr>
<td></td>
<td>1:1</td>
<td>2.91</td>
<td>2.10</td>
<td>2.14</td>
<td>2.88</td>
<td></td>
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<tr>
<td></td>
<td>0.45:1</td>
<td>1.92</td>
<td>1.60</td>
<td>1.60</td>
<td>1.80</td>
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</tbody>
</table>

* Three replicates. Standard deviation ± 0.05. Sucrose/starch ratio of 0.41; NaCl/starch ratio of 0.041; and surfactant/starch ratio of 0.0041.
* Myvaplex 600, a commercial surfactant containing at least 90% glyceryl monostearate.

### CONCLUSION

In the presence of sucrose or sodium chloride, gelatinization temperatures of rice flour or starch suspension shifted to higher temperatures and enthalpy decreased. As expected, the effect of the presence of solutes in the system was more pronounced in a limited-water system. The effect of sucrose on gelatinization temperature could be explained by considering starch as a partially crystalline glassy polymer as suggested by Maurice et al. (1983) and subsequent analysis by Biladeris et al. (1986). The effect of sodium chloride was consistent with observations and an explanation proposed by Oosten (1982). Surfactant had a slight effect on gelatinization temperatures and had no effect on enthalpy of
gelatinization. No difference was observed between the gelatinization characteristics of flours and their isolated starch counterparts. Moreover, qualitatively both rice samples behaved similarly even though there were slight differences in amylose content. Microscopic examination using a polarized light microscope confirmed the observations obtained from DSC.

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