Parboiling of rice. Part II: Effect of hot soaking time on the degree of starch gelatinization

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Summary

A differential scanning calorimetric study was done on raw and parboiled rice to determine the degree of gelatinization. Unparboiled rice absorbed the highest amount of endothermic heat, the enthalpy change gradually decreasing with increasing hot soaking time. The highest degree of gelatinization was achieved when the paddy was soaked for 120 min at 80 °C. With increasing degree of gelatinization, the yield point in a compression test also increased. During the parboiling process internal fissures were healed, resulting in higher head rice yield during milling.

Keywords

Colour, darkness, differential scanning calorimetry (DSC), enthalpy, relative darkness, yield point.

Introduction

The three steps of parboiling – soaking, steaming and drying are generally achieved by soaking paddy in cold water for typically 24–48 h until the kernels are saturated. The soaked paddy is then boiled at c. 100 °C for typically 1 h to obtain 80% gelatinized starch (Priestley, 1976a). Finally the boiled paddy is sun-dried until the moisture content is reduced to c. 14%.

The degree of starch gelatinization is responsible for many of the attributes of parboiled rice (Marshall et al., 1993). During the process of gelatinization, amylose molecules leach out of the micellar network and diffuse into the surrounding aqueous medium outside the granules (e.g. Hermansson & Svegmark, 1996). The granules become fully hydrated, producing a maximum in the measured viscosity (Eliasson, 1986).

The temperature at which rapid swelling starts is known as the gelatinization onset temperature and the halfway transition temperature is called the transition midpoint temperature, $T_m$. The changes that occur upon cooling and storage of gelatinized starch because of gradual reordering of amylopectin and the intermolecular association between amylose molecules is termed as retrogradation.

Marshall et al. (1993) reported that incomplete parboiling result in partial surface starch gelatinization. The dried kernels produced translucent outer layers and an opaque or white centre from the non-gelatinized starch. Completely gelatinized parboiled rice kernels are translucent.

Although the effectiveness of parboiling in improving the quality of milled rice is well known (Bhattacharya & Subba Rao, 1966a,b; Priestley, 1976a,b; Juliano et al., 1981; Marshall et al., 1993), the effects of gelatinization on milling qualities have not yet been quantified. This study was therefore undertaken to investigate the effects of the degree of gelatinization on milling qualities by varying the hot soaking time during parboiling, and to establish the relationship between these parameters.

Materials and methods

Following the methodology described in Part I (Miah et al., 2002) a high yielding long grain rice variety (BR4), developed by the Bangladesh Rice Research Institute was harvested, the grains separated from panicles by the drum beating method and then dried in the sun until the moisture content was...
c. 14%. The amylose content for this rice variety is 25% (Biswas et al., 1992). The paddy was stored at 25 °C in sealed polythene bags until use.

Differential scanning calorimetry

The formation and dissociation of ordered structures is normally accompanied by enthalpy changes that can be detected by sensitive calorimetric measurements (Wright, 1984). Where the molecular changes are induced by changes in temperature the appropriate technique is differential scanning calorimetry (DSC). A Setaram microcalorimeter (model – Micro DSC II, Setaram, Caluire, France) equipped with a plotter was used to obtain endothermic heat flow. A coffee grinder was used for grinding milled rice samples, followed by mortar and pestle grinding to make the particles finer. The particles mainly fell within the range of 100–300 microns.

Samples of about 950 mg (water + rice flour), with water as the reference, were loaded into 1 mL tantalum ampoules. Sample and reference pans were balanced within 1 mg. Rice flour samples (30% flour, 70% water, w/w) from 15, 30, 45, 60 and 120 min hot soaked paddy were scanned from 35 to 98 °C at a heating rate of 1 °C min\(^{-1}\). A sample of raw rice flour (without parboiling treatment) was also included as a control. All samples were then cooled at the same cooling rate to observe any thermal transition on cooling the gelatinized starch. A ratio of 1:2.33 between milled rice grain and water provides a moisture content of 70% in the cooked rice. At this moisture level all the starch granules in the rice flour are fully cooked and gelatinized (Juliano et al., 1981). The guidelines from Juliano et al. (1981) were adopted to determine the concentration of rice flour for this DSC study. However, different concentrations of rice flour as well as different rates of heating were also used for comparison.

The degree of starch gelatinization was determined by comparing the enthalpy change of parboiled rice (\(\Delta H_{par}\)) to that of raw rice (\(\Delta H_{raw}\)) as described by Marshall et al. (1993). Therefore the following calculations were made:

\[
\text{Ungelatinized starch (\%) = } \left( \frac{\Delta H_{par}}{\Delta H_{raw}} \right) \times 100
\]

or

\[
\text{starch gelatinization (\%) } = \left[ 1 - \left( \frac{\Delta H_{par}}{\Delta H_{raw}} \right) \right] \times 100
\]

Subjective grading of parboiled rice

Samples of 150 g were dehusked and polished as previously described. The milled sample was sieved and the head rice collected. Representative samples (150–200 grains) were then obtained using the riffle box. A magnifying glass was used to separate the translucent kernels from the representative sample. Finally, the percentage of translucent grain was calculated from the ratio of the number of translucent grains to the total number of grains. All treatments were replicated three times.

Yield point determination

The yield point was determined by an Instron tester (model 1122; Instron Ltd, High Wycombe, Bucks, UK), having a 500 N load cell with automatic loading rate and chart plotting facility. Individual grains with husk were placed on a flat plate and crushed with a flat probe of 12-mm diameter fixed parallel to the base, at a cross-head speed of 1 mm min\(^{-1}\). Force at rupture (first breaking) was considered as the yield point and recorded for each run. Six replications were conducted for each treatment and the measured forces were averaged.

Relative darkness

Relative darkness was determined by measuring the intensity of reflected light from the surface of the polished grains using a Minolta Chromameter (model CR-200b; Minolta Co Ltd, Milton Keynes, UK). The meter was calibrated with a standard white surface of brightness index 93. The relative darkness of different degrees of gelatinized milled rice was assessed based on this index.

Results and discussion

Differential scanning calorimetry

Effects of soaking on gelatinization enthalpy and mid-transition temperature \(T_m\)

Figure 1 shows illustrative DSC plots for 30% flour samples of raw and parboiled rice on heating
at 1 °C min⁻¹. All six samples produced a single endotherm on heating. The heating scans for all the samples, representing different degrees of hot soaking, were virtually identical in shape, with the thermal transition for raw rice (assumed to be fully ungelatinized) occurring about 5 °C earlier than other treatments. However, the size of the peaks (and hence, the enthalpy values of the ungelatinized starch) gradually decreased with increase in soaking time, from no soaking for raw rice to 120-min soaking for parboiled rice. At the highest degree of soaking, a gelatinization enthalpy of 0.86 J g⁻¹ of parboiled rice flour was obtained (in comparison with 6.03 J g⁻¹ for raw rice flour), indicating from equation (1) that 14% of the starch remained ungelatinized after 120 min of soaking. Scanning at 1 °C min⁻¹ using a 30% concentration of rice flour, the transition midpoint temperatures (T_m), gelatinization enthalpies (ΔH) and degrees of starch gelatinization for different hot soaking treatments are listed in Table 1.

Figure 2 shows the relationship between hot soaking time during the parboiling of paddy and the percentages of starch gelatinization. The corresponding T_m values are also shown. A third-order polynomial gave the best regression fit throughout the starch gelatinization data. All the parboiled rice flour samples produced T_m values between 83 and 84.2 °C, the data can be represented by a linear fit of negligible positive slope (0.0099). The raw sample had an appreciably lower T_m of 78.5 °C. As reported by Normand & Marshall (1989), a similar T_m (75.9 °C) was observed for a rice variety of the same amylose content (25%). The corresponding gelatinization enthalpy, ΔH = 10.3 J g⁻¹, reported by Normand & Marshall (1989), was higher than the results from this study (Fig. 5). However, they did not report the age of the rice after harvesting, which has a great influence on enthalpy. In a separate study on ageing, an increase in gelatinization enthalpy was observed with increasing ageing (data not shown).
Samples soaked at 80 °C for 15, 30, 45, 60 and 120 min were scanned in the DSC, and the highest gelatinization value of 86% was found after 120 min of hot soaking. During this partial gelatinization it is thought that the diffused amylase molecules reorientated and surrounded the amylpectin granules (which were already swollen by the penetration of water molecules), and subsequently retrograded on cooling and storage. These processes changed the original network of the intact granules and, on reheating, this amylase structure outside the granule inhibits subsequent swelling of water at the temperature where unparboiled rice starch swelled. Biliaderis et al. (1986) proposed a process of partial melting followed by recrystallization during cooling and subsequent storage. This explains the delayed onset of gelatinization (and hence, the $T_m$) for all the parboiled rice flour samples (Figs 1 and 2).

**Heat transfer effect**

The effect of heating rates on gelatinization temperature and enthalpy are shown in Fig. 3. Both the transition-midpoint temperatures and enthalpy of gelatinization were extrapolated at 0 scanrate to eliminate the effect of heat transfer. The transition-midpoint temperatures for both raw and parboiled rice (30% w/w) decreased gradually on decreasing heating rate, with significant variation between them within the same scanrates. The slope of the straight line fit for parboiled rice, however, was slightly higher (slope = 5.87) than that of raw rice (slope = 5.04), narrowing the difference between them at zero heating rate. As indicated in the graph, parboiled rice experienced a higher $T_m$ of c. 4 °C at zero scan-rate ($T_m = 73.4$ for raw compared with $T_m = 77.1$ °C for 15-min hot soaked parboiled rice).

The corresponding enthalpy changes for both raw and parboiled rice increased with decreasing heating rate (Fig. 3), which is in good agreement with the findings of Normand & Marshal (1989). Raw rice shows significant variation within the scan-rates, producing about a 1.75-fold higher slope compared with parboiled rice, giving extrapolated enthalpies of 8.16 and 5.76 J g$^{-1}$ at 0 scanrates for raw and parboiled rice, respectively. The higher slope for raw rice clearly indicates that the release of amylase molecules and subsequent swelling of (ordered) amylpectin are dependent on the rate of heating.

**Effect of starch concentration on gelatinization enthalpy and $T_m$**

The ratio of starch and water plays a significant role in the behaviour of gelatinization (Fig. 4). The onset of gelatinization starts at about the same temperature but completion (and hence, the

![Figure 3](image-url) DSC scan-rate dependence of transition midpoint temperature ($T_m$) and enthalpy changes ($\Delta H$) for raw (●) and 15-min hot soaked parboiled paddy (○) at 30% (w/w) concentration of rice flour.

![Figure 4](image-url) DSC traces, after base-line correction, for raw paddy at concentrations of 1, 10, 30 and 50% at a heating rate of 1 °C min$^{-1}$.
$T_m$) increases with increasing starch concentration (Fig. 5). This behaviour agrees with the findings by BeMiller (1993). Enthalpy of gelatinization decreases with increasing starch/water ratio in a linear fashion. A likely explanation is that during endothermic processes, the lower concentration provides the starch granules with more opportunity to absorb heat through the diffusion process. In other words, at low concentrations of starch, amylase molecules leach out more freely allowing penetration of water to the amylopectin, resulting in higher intake of heat (and hence, higher enthalpy). At higher concentrations, on the other hand, starch granules cannot absorb heat so readily because of the congestion of granules, resulting in a lower enthalpy value.

**Compressive strength of paddy**

Figure 6a shows a linear relationship ($r^2 = 0.971$) between the compressive force at rupture (yield point) and the soaking time. The most likely explanation is that, with the increase of hot soaking time during parboiling, individual grains gelatinized more and on retrogradation, the grains become more resistant to break, producing a positive linear slope of $\approx 0.6$. Plotting the same force data, however, against the degree of gelatinization produces obvious curvature (Fig. 6b) which is fitted reasonably well ($r^2 = 0.982$) by a third order polynomial.

**Comparison between subjective and objective methods**

Figure 7 shows the relationship between the degree of soaking (and hence the degree of
gelatinization) and the percentage of translucent kernels for raw and parboiled rice. When the gelatinization of starch increased above 57% (obtained after 45-min soaking), opaque grains started losing their opacity and translucent grains appeared. The highest percentage of translucent grains (26%) was obtained with parboiled paddy soaked for 120 min, while there was no grain found translucent below 45-min soaking. This result is in good agreement with what Marshall et al. (1993) found, and explains why a slurry of starch paste is opaque on partial gelatinization and become clear on further heating to complete gelatinization (Eliasson, 1986).

Effect of gelatinization on the relative darkness of milled rice

Generally, the colour of parboiled rice has a definite bearing on its quality in terms of consumers’ preference and thus value in the market. Rapid cooling of the steamed paddy is necessary if soft cooking quality and desired colour is required because slow cooling would produce harder rice with much darker colour (Bhattacharya & Subba Rao, 1966b). The hot soaking time has a definite effect on the colour development. The colour-inducing effect is chiefly because of nonenzymatic browning by the Maillard reaction. Sugar released during the parboiling process reacts with the amino acids of the grain, causing discoloration of milled rice. The bran and husk pigments might also contribute by diffusing into the endosperm during soaking (Patil et al., 1982). The relationship between the degree of gelatinization and the relative darkness of milled rice is shown in Fig. 8. On parboiling with different degrees of soaking (and hence gelatinization), the relative darkness gradually increased from 23 to 36. A minimum of 45-min soaking at 80°C was adequate for acceptable darkness, corresponding to a value of 34 (not far from the maximum value of 36). This was close to the relative darkness of 35, obtained for Sainsbury’s Uncle Ben’s (a commercial parboiled rice).

Conclusions

The degree of gelatinization of starch, a physical, chemical and biological parameter of great importance in milled rice quality, was determined and found to increase on increasing the duration of hot soaking. The DSC endothermic heat flow (ΔH) of rice starch was found to be dependent on soaking duration. When the heating rate and polymer concentrations were decreased, the
gelatinization enthalpy values were found to be increased. The effect of gelatinization on parboiling made the grain stronger, which improved milling qualities.

One important factor for consumer preference is physical appearance, in particular, translucency, and this was greatly improved by using longer hot soaking treatment producing a gelatinization of above 57%. The extent of darkness, the other criteria for consumer preference, was also improved by extending the hot soaking time.

Finally, it may be concluded that a minimum of about 45-min soaking at 80 °C followed by steaming for about 10 min under 1 atmosphere excess pressure is necessary to improve all the required qualities of rice for better consumer preference. These figures are the recommendation that can be made to the rice millers to improve the milling quality of parboiled rice, as well as increasing the rate of supply by reducing the soaking time from 24–48 h to 45–120 min.

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References


