Glassy State Transition and Rice Drying: Development of a Brown Rice State Diagram

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T. J. Siebenmorgen, and A. Mauromoustakos

The effect of moisture content (MC) on the glass transition temperature (Tg) of individual brown rice kernels of Bengal, a medium-grain cultivar, and Cypress, a long-grain cultivar, was studied. Three methods were investigated for measuring Tg: differential scanning calorimetry (DSC), thermomechanical analysis (TMA), and dynamic mechanical analysis (DMA). Among these methods, TMA was chosen, because it can also measure changes in the thermal volumetric coefficient (β) of the kernel during glass transition. TMA-measured Tg at similar MC levels for both cultivars were not significantly different and were combined to generate a brown rice state diagram. Individual kernel Tg for both cultivars increased from 22 to 58°C as MC decreased from 27 to 3% wb. Linear and sigmoid models were derived to relate Tg to MC. The linear model was sufficient to describe the property changes in the MC range encountered during rice drying. Mean β values across both cultivars in the rubbery state were 4.62 × 10⁻⁴/K and was higher than the mean β value of 0.87 × 10⁻⁴/K in the glassy state. A hypothetical rice drying process was mapped onto the combined state diagram generated for Bengal and Cypress.

In the United States, rice is usually harvested at =16–22% moisture content (MC) (wb) and must be dried to =12% MC for safe storage. Drastic drying conditions and subsequent exposure of the dried kernels to air at high relative humidity can increase the number of fissured kernels (Kunze and Prasad 1978, Kunze 1979, Sharma and Kunze 1982). Proposed theories on fissure formation are based on the response of rice when subjected to tensile and compressive stresses due to the existence of a moisture gradient within the kernel (Kunze and Choudhury 1972, Kobayashi et al 1976, Yamaguchi et al 1980).

The effect of water on rice thermal and physical properties is a key in understanding the drying process (Watten et al 1969, Arora et al 1973, Morita and Singh 1979, Steffe and Singh 1980, Muthukumarappan et al 1992). Watten et al (1969) showed that the physical properties (length, width, thickness, volume, density, and specific gravity) and thermal properties (specific heat and thermal conductivity) of long- and medium-grain rice were linear functions of MC. Morita and Singh (1979) also found that short-grain rough rice kernel dimensions, bulk density, and specific gravity varied linearly with MC at 26°C. Short-grain rice shrunk by an average of 12.3% when dried from 30 to 15% MC (Steffe and Singh 1980). Rough rice showed lower coefficients of volumetric expansion than brown and milled rice at room temperature. The volumetric reduction of the rice hull was significantly lower than that of the other parts of the rice kernel.

Rice properties are also affected by kernel temperature. Arora et al (1973) reported an increase in milled rice thermal expansion at >53°C and showed that more rice kernels fissure above this transition temperature. Muthukumarappan et al (1992) measured volumetric changes in long-grain rice during moisture desorption and adsorption. In their measurements, the coefficients of linear hygroscopic expansion were greater across grain thickness than with either kernel length or width during adsorption and desorption. During desorption, brown rice had a greater coefficient of linear expansion compared with roughs and milled rice. However, milled rice had a higher coefficient of cubical thermal expansion than rough and brown rice. The rate of thermal expansion of rice was uniform at ≤58°C. However, Muthukumarappan et al (1992) assumed that thermal expansion at >60°C was not important, and they used a single rate in their model for rice drying.

Integrating the effects of water and temperature on material property changes is important in understanding fissure formation during grain drying. Polymer science has been applied in studying the effect of temperature and MC changes during processing on food components such as starch and protein (Slade and Levine 1991a,b, 1993, 1995; Levine and Slade 1992; Kokini et al 1994; Roos 1995; Madeka and Kokini 1996; Strahm 1998). In a review of rice milling, Rhind (1962) suggested that starch, the main constituent of rice, is brittle at <15% MC but is plastic at higher MC levels. In food polymer science terms, starch is considered a partially crystalline, partially amorphous polymer of glucose, whose properties change depending on temperature and MC (Slade and Levine 1991a,b, 1995). Within the starch granule, amylase and the branching points of amylopectin contribute to the amorphous phase, while the outer chains of amylopectin contribute to the crystalline phase. Changes in the crystalline region occur during processing at high MC (>25–28%) or high temperatures (>70°C). At lower MC and temperatures, conditions applicable during rice drying, most of the changes occur in the amorphous region. Physical and thermal properties of amorphous solids such as specific heat, specific volume, expansion coefficients, and elastic modulus change as the solid goes through a glass transition temperature (Tg) (White and Cakir 1966). At temperatures below Tg, amorphous materials are glassy, with high viscosity and modulus of elasticity but low specific heat, specific volume, and expansion coefficient. At temperatures above Tg, these materials are rubbery, with much higher specific heat, specific volume, and expansion coefficient.

Moisture content changes during processing affect the thermal properties of a food system. Water is a very effective plasticizer and will reduce Tg (as MC increases, Tg decreases) (Slade and Levine 1991b). Plotting Tg against corresponding MC will generate a state diagram that can be used to predict the mechanical properties of an amorphous solid at a particular temperature and MC (Levine and Slade 1992). The temperature of the material relative to Tg, which is governed by MC, will determine whether the material will be in the glassy solid or rubbery liquid state (Slade and Levine 1991b). State diagrams and the concept of glass transition have been applied to predict changes in food properties and reaction kinetics below and above Tg (Roos and Karel 1991; Slade and Levine 1991a, 1995; Nelson and Labuza 1994; Roos 1995; Peleg 1992, 1996).

Mathematical models have been developed to predict drying and MC curves for grain and pasta (Fortes and Okos 1981a,b; Litchfield and Okos 1992; Achanta et al 1995). The diffusion model of Litchfield and Okos (1992) for pasta successfully predicted the
drying curve and MC profile at 40°C, but underpredicted both at higher temperatures and lower humidities. The discrepancy in their data may have been due to pasta changing from a glassy to a rubbery state at ~40°C. The contribution of the rubbery to glassy transition to structural shrinkage was accounted for in a later model (Achant et al. 1995), and this model reasonably predicted the drying curve and MC profile for starch-gluten gel at 22 and 40°C.

Reaction kinetics depend on whether a material is in the glassy or the rubbery state (Peleg 1996). Models describing changes in an amorphous system need to account for the different kinetics below and above \( T_g \). To understand rice kernel fissuring, drying kinetics at and around \( T_g \) need to be investigated. Only a few studies on changes in thermal properties of rice at >25% MC have been published. Among these, Nehus (1997) measured milled rice thermal properties with a differential scanning calorimeter and reported that rice at 16–18% MC has a \( T_g \) of 55°C. The transition point between 50 and 60°C found by Arora et al (1973) and Muthukumarappan et al (1992) may be the \( T_g \) identified by Nehus (1997). If so, a glassy to rubbery state transition occurring within this temperature range, typically encountered during drying, would affect the kinetics and material property changes in a rice kernel.

Rice kernel MC and temperature during drying will determine mechanical properties. Existence of a temperature or MC gradient within a kernel may generate regions with different mechanical properties such as different expansion coefficients or specific volumes. The differences in these properties may create stresses sufficient to fissure the kernel.

An overall goal of the University of Arkansas’ Rice Processing Program, in the area of rice drying, is to understand the fundamental mechanism of fissure development in a rice kernel during the drying process by integrating numerical modeling with polymer science. The objectives of this study were to measure the \( T_g \) of a medium- and a long-grain rice cultivar dried to different MC levels, and to generate a state diagram for mapping a typical rice drying process. The volumetric expansion coefficients (\( \beta \)) below \( T_g \) (glassy region) and above \( T_g \) (rubbery region), of these two cultivars at different MC levels were also measured. These results were the basis for formulating a hypothesis to explain rice fissure formation during the drying process.

**MATERIALS AND METHODS**

**Rough Rice Collection and Preparation**

Multiple samples of rice cultivars Bengal, with harvest MC levels of 16, 17, and 22% (wb), and Cypress, with harvest MC levels of 16, 20, and 22% (wb), were harvested in 1997 from the University of Arkansas Rice Research and Extension Center at Stuttgart, AR. Bengal is a medium-grain cultivar with a low amylose content, and Cypress is a long-grain cultivar with a high amylose content. Immediately after harvest, the rough rice samples from each cultivar were cleaned (Dockage Tester, Carter-Day, Co., Minneapolis, MN).

Each cleaned rough rice lot was dried to different MC levels in chambers with controlled air temperature and relative humidity (rh) (300-CFM Climate-Lab-AA model AA-5460A, Parameter Generation & Control, Black Mountain, NC) to generate different equilibrium moisture contents (EMC): 60°C and 17% rh, 51°C and 25% rh, and 43°C and 38% rh. EMC were calculated using Ching’s equation (ASAE 1991). Samples with bulk MC of 5–22% were removed after different drying durations. These samples were placed in sealed plastic bags and stored at 4°C for at least 24 hr before further analysis. The MC of each rough rice sample was analyzed by drying duplicate samples for 24 hr in an air-oven set at 130°C (Jindal and Siebenmorgen 1987). Total samples collected at different MC levels were 120 for Bengal and 108 for Cypress.

Samples of rough rice at each original harvest MC (Bengal: 16, 17, and 22% MC; Cypress: 16, 20, and 22% MC) were conditioned directly to 12.5% MC in a conditioning chamber set at 21°C and 53% rh. Proximate compositions of brown rice from each cultivar were analyzed. Brown rice was prepared by dehulling each conditioned rough rice sample in a McGill sample sheller (Rapsco, Brookshire, TX). The dehulled rice was ground in a Cyclotec mill (Udy Corp., Fort Collins, CO) fitted with a 0.5-mm screen. Starch content was measured according to AACC Method 76-11 (AACC 2000). The apparent brown rice amylose content was analyzed following the method described by Juliano (1971). Protein content was measured using the Kjeldahl method (AACC 2000).

**Individual Kernel Thermal Properties**

Individual kernel sections, instead of rice flour, were used for thermal and volumetric expansion coefficient measurements to account for the natural variability in size and individual kernel MC distribution existing among rice kernels at particular bulk MC levels.

Rice kernels were randomly sampled at least in duplicate from each rough rice sample and hand-dehulled. The \( T_g \) of each brown rice kernel was measured with differential scanning calorimetry (DSC) (Pyris 1 equipped with an Intracooler II, Perkin-Elmer, Norwalk, CT). The DSC equipment was calibrated with indium \((T_m = 156.6°C \text{ and } \Delta H = 28 \text{ J/g})\). Before each analysis, the dimensions (length, width, thickness) of the kernel were measured with a vernier caliper. Each kernel was cross-sectioned into three parts with a razor blade. The three sections were placed in preweighed high-pressure stainless steel pans and sealed. The pan was weighed to obtain the sample weight. A sealed empty high-pressure stainless steel pan was used as the reference. The sample was equilibrated to –50°C for 5 min and then heated from –50 to 250°C at a rate of 10°C/min. The \( T_g \) from each thermogram was determined by identifying the transition corresponding to a slope change in the heat capacity of the sample.

Brown rice \( T_g \) was also measured with thermomechanical analysis (TMA) (TMA7, Perkin-Elmer), cooled with a dry-ice and ethanol mixture. In addition to accurate measurement of \( T_g \), critical material property changes occurring below and above \( T_g \) can be measured with TMA. The length, width, and thickness of a given whole brown rice kernel were measured with a vernier caliper. The whole kernel was placed in a preweighed small quartz dilatometer (7.1-mm i.d., Perkin-Elmer N519-0763) and the total mass was determined. The dilatometer was filled with aluminum oxide (Al2O3), covered, and reweighed. The dilatometer was placed in the sample holder of the TMA equipment, and an expansion probe was used to record volume change in the sample during heating (Anonymous 1995). The sample was held isothermally at ~15°C for 5 min and then heated from ~15 to 65°C at a rate of 5°C/min. The temperature at which the volume drastically changed was taken as \( T_g \). Software was used to identify \( T_g \) and calculate the expansion coefficients from the thermogram (Perkin-Elmer thermal analysis software ver. 4.00). In the sample thermogram (Fig. 1), \( T_g \) is the temperature where tangent lines, drawn along the two regions with differing slopes, intersect. The locations of the glassy and rubbery regions are also illustrated in Fig. 1. The coefficients of volumetric expansion in the glassy region \((\beta_{glassy})\) and the rubbery region \((\beta_{rubbery})\) were computed by multiplying the expansion coefficients calculated for each region by the cross-sectional area of the dilatometer (0.3941 mm²). After testing, each kernel was reweighed to determine moisture loss. The MC of each kernel was subsequently analyzed by placing the kernel in a porcelain spot plate and drying the sample for 2 hr in an air-oven set at 130°C.

Variabilities in \( T_g \) and \( \beta \) measurements were observed during preliminary TMA experiments. The effect of Al2O3 used in the dilatometer and of the TMA heating rate on \( T_g \) and \( \beta \) of individual brown rice kernels for both cultivars at 20–22% MC was tested. Measurements using the Al2O3 included in the dilatometer kit (Perkin-Elmer No. 419-0197) were compared with Al2O3 prepared in the laboratory by mixing five parts of Al2O3 (A591-500, Lot 972444, Fisher Scientific, Hampton, NH) with one part of mineral oil (400-5, Lot 0478H6080, Sigma Chemical Co., St. Louis, MO).
At least 36 measurements using Bengal were done for each type of Al\textsubscript{2}O\textsubscript{3}. With the use of the Al\textsubscript{2}O\textsubscript{3} prepared in our laboratory, the effects of heating 36 Bengal brown rice kernels at 2, 5, and 10°C/min on the different thermal properties were tested.

The standard error associated with the \( T_g \) measurement of rice kernels, which are heterogeneous, using TMA was compared with the standard error associated with the \( T_g \) measurement of amorphous sucrose, which is homogeneous. Amorphous sucrose was prepared by dissolving two parts of sucrose in one part of deionized water. The syrup was heated to 120°C, poured onto aluminum pans, and allowed to harden by cooling to room temperature. Six small pieces (25–50 mg) of the sugar glass (10–11% MC) were analyzed for \( T_g \) as described previously.

To confirm that the brown rice kernel \( T_g \) range determined with the TMA was due to glass transition and not air expansion, the changes in elastic modulus of a limited number of kernels were also analyzed using dynamic mechanical analysis (DMA). The brown rice \( T_g \) of at least three kernels each from Bengal and Cypress at 20–22% MC was checked using a dynamic mechanical analyzer (DMA 7e equipped with an Intracooler II, Perkin-Elmer). A three-point bend platform was used, and the modulus of elasticity was measured from 0 to 70°C at 5°C/min. The onset temperature of the drop in modulus was taken as \( T_g \) (Anonymous 1995).

### Statistical Analysis

The study was treated as a completely randomized design. All statistical analyses were performed using JMP (SAS Institute, Cary, NC). Distribution profiles of kernel dimensions and proximate compositions were obtained. Analysis of variance was applied to determine the standard errors associated with \( T_g \) and \( \beta \) measurements. Pearson product-moment correlations between DSC-measured \( T_g \) and MC were analyzed. Results with \( P \leq 0.05 \) were considered to be significant. Separate state diagrams were constructed for Bengal and Cypress by plotting the TMA-measured \( T_g \) of the individual kernels against the corresponding MC. Linear and nonlinear models describing the relationship of \( T_g \) to MC for each cultivar were developed using JMP. The effect of cultivar on the models was tested to determine whether a single linear or nonlinear model could represent the relationship of \( T_g \) to MC.

### RESULTS AND DISCUSSION

The proximate composition and mean kernel dimensions of Bengal and Cypress are shown in Table I. They were consistent with respective rice types. The starch levels of the two cultivars were comparable, but the protein content of Cypress was significantly higher than that of Bengal. Bengal, a medium-grain cultivar, had lower amylose content compared with Cypress, a long-grain cultivar. These amylose differences reflect differences in the amylose/amylopectin ratio of the samples and could have had an effect on the degree of crystallinity of the rice starch and, consequently, thermal properties.

### DSC Measurement of \( T_g \)

As mentioned earlier, individual kernels were used for thermal and volumetric expansion coefficient measurements to account for the natural variability in size and individual kernel MC distribution among rice kernels at particular bulk MC levels. In spite of this precaution, characterization of brown rice thermal properties using DSC was complicated by the appearance of apparent multiple second-order transitions. The DSC thermogram in Fig. 2 for Bengal brown rice at 12% MC showed three noticeable transitions at \(-5, 55, \) and \(70^\circ\text{C} \). Multiple transitions were found in almost all of the thermograms for Bengal and Cypress at MC levels ranging from 12 to 22%.

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from 10 to 25%. Biladeris (1991) also observed several transitions in the DSC thermograms for rice starches from different cultivars. Rice kernel morphology is very heterogeneous, and some regions may be more amorphous and less crystalline than others. This may be the result of different conformatations and interactions between amylose, amylopectin, and other rice components such as proteins and lipids.

The temperatures of the three transitions and the starch melt \( (T_m) \) were plotted against corresponding MC for Bengal brown rice kernels (Fig. 3). As expected, \( T_m \) decreased as MC increased, and the correlation was significant \( (r = -0.92, P < 0.01) \). Moisture content did not affect the transition occurring around \(-5^\circ\)C and \(70^\circ\)C. The correlations at these temperatures were \( r = -0.23 \) \( (P = 0.30) \) and \( r = -0.20 \) \( (P = 0.38) \), respectively. The transition occurring at \(16^-57^\circ\)C showed a strong correlation \( (r = 0.75, P < 0.01) \) with MC. This indicated that the transition occurring in this temperature range was sensitive to changes in MC and might be where glass transition occurred. Nehus (1997), using DSC, also reported transitions at \(\approx 50^\circ\)C in milled rice at 12–16% MC. Cypress brown rice showed similar results.

**TMA Measurement of \( T_g \)**

In addition to accurate measurement of \( T_g \), critical material property changes occurring below and above \( T_g \) needed to be identified using TMA. The TMA procedure was optimized by identifying the type of \( \text{Al}_2\text{O}_3 \) and heating rate that gave the lowest variability in \( T_g \) and \( \beta \) of samples harvested at >20% MC. Analysis of variance showed that the type of \( \text{Al}_2\text{O}_3 \) used did not have a significant effect on \( T_g \), \( \beta_{\text{glassy}} \), and \( \beta_{\text{rubbery}} \) \( (P = 0.10, 0.66, \) and 0.91, respectively). However, examination of the \( T_g \) and \( \beta \) measurements showed that the \( \text{Al}_2\text{O}_3 \) prepared in our laboratory resulted in lower standard errors than the \( \text{Al}_2\text{O}_3 \) from Perkin-Elmer (Table II). In addition, the mean kernel moisture loss was lower for the \( \text{Al}_2\text{O}_3 \) prepared in our laboratory, 0.6 percentage points compared with 1.6 percentage points for \( \text{Al}_2\text{O}_3 \) from Perkin-Elmer. The finer particle size of the laboratory-prepared \( \text{Al}_2\text{O}_3 \) (79% of the particles were <90 µm), compared with Perkin-Elmer (67% were <90 µm), may have contributed to the lower standard errors for the \( T_g \) and \( \beta \) measurements.

The effect of three heating rates (2, 5, and \(10^\circ\)C/min) on \( T_g \) and \( \beta \) of rice kernels harvested at >20% MC was tested. Heating rate affected the measurement of \( T_g \) \( (P < 0.01) \) but not \( \beta \) \( (P = 0.81 \) and 0.50 for \( \beta_{\text{glassy}} \) and \( \beta_{\text{rubbery}} \), respectively). The mean \( T_g \) at a heating rate of \(2^\circ\)C/min was \(28.9^\circ\)C and was not significantly different than what would typically be expected due to the kinetic nature of the glass transition [Slade and Levine 1991a] could have been due to a greater thermal lag at the fastest heating rate. The \(5^\circ\)C/min heating rate and the laboratory-prepared \( \text{Al}_2\text{O}_3 \) were used for subsequent TMA experiments.

Amorphous sucrose (<10% MC, wb), which was considered to be more homogeneous than a brown rice kernel in terms of composition, was used to determine the standard error associated with measuring \( T_g \) using TMA. The mean \( T_g \) \( (n = 6) \) was \(37.5^\circ\)C with a standard error of 0.22. This standard error for amorphous sucrose was lower than those observed for the \( T_g \) of individual brown rice kernels, where the standard error for Bengal \( (n = 120) \) was 0.53 and for Cypress \( (n = 100) \) was 0.63.

Later experiments showed wide variabilities in the \( T_g \) of individual brown rice kernels taken from the same panicle. The standard error decreased from 3.3 for Bengal harvested at >22% MC to 0.5 for Bengal harvested at 18% MC. These results reflect the increased variability in kernel MC and size at high harvest MC (Kocher et al. 1990). This experiment demonstrated that the variabilities observed in \( T_g \) were primarily due to sample heterogeneity and not to the method.

Figure 1 shows a typical TMA thermogram for brown rice, with \( T_g \) and the locations of the different regions around \( T_g \) identified. The plots of individual brown rice kernel \( T_g \) (17–58°C) for Bengal and Cypress against corresponding MC (3–27%) are shown in Fig. 4. As expected, individual kernel \( T_g \) for both Bengal and Cypress increased as MC decreased. The correlation of \( T_g \) with MC was significant: \(-0.73 \) and \(-0.62 \) for Bengal and Cypress, respectively \( (P < 0.01) \). An overall correlation of \(-0.68 \) \( (P < 0.01) \) was obtained by pooling the data for both cultivars.

The temperature range, over which the elastic moduli of individual brown rice kernels from Bengal and Cypress decreased, was measured using DMA. At 20–22% MC, the elastic modulus of the kernels varied at 15.5–59°C, with a mean at \(40^\circ\)C \( (n = 6) \). This was comparable to the temperature range over which the kernels showed increases in \( \beta \) using TMA, and verified that the transitions measured with TMA were due to glass transition and not air expansion. In addition, this temperature range encompassed the \( T_g \) that Nehus (1997) reported for milled rice at 16–18% MC, as well as the transition points identified by Arora et al (1973) and Muthukumarappan et al (1992).

**Coefficient of Thermal Volumetric Expansion**

The mean \( \beta \) as measured with TMA, for individual kernels of both cultivars undergoing glass transition are shown in Table III. The mean \( \beta_{\text{rubbery}} \) was \(4.6 \times 10^{-4}/\circ\)C, which is within the range of brown rice cubical thermal expansion coefficients reported by Arora et al (1972) and Muthukumarappan et al (1992), \(3.4 \times 10^{-4}/\circ\)C and \(5 \times 10^{-4}/\circ\)C, respectively.

**TABLE II**

<table>
<thead>
<tr>
<th>( \text{Al}_2\text{O}_3 )</th>
<th>( T_g ) (°C)</th>
<th>( \beta_{\text{glassy}} ) ( \left(10^{-4}/\circ)C\right) )</th>
<th>( \beta_{\text{rubbery}} ) ( \left(10^{-4}/\circ)C\right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perkin-Elmer ((n = 43))</td>
<td>0.81</td>
<td>0.07</td>
<td>0.32</td>
</tr>
<tr>
<td>Laboratory prepared ((n = 35))</td>
<td>0.51</td>
<td>0.05</td>
<td>0.15</td>
</tr>
</tbody>
</table>

* Using different aluminum oxide types.

**TABLE III**

<table>
<thead>
<tr>
<th>Cultivar</th>
<th>( \beta_{\text{glassy}} ) ( \left(10^{-4}/\circ)C) )</th>
<th>( \beta_{\text{rubbery}} ) ( \left(10^{-4}/\circ)C) )</th>
<th>( \beta_{\text{rubbery}}/\beta_{\text{glassy}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bengal ((n = 120))</td>
<td>0.86a ( (0.04) )</td>
<td>4.99a ( (0.17) )</td>
<td>5.80a</td>
</tr>
<tr>
<td>Cypress ((n = 100))</td>
<td>0.89a ( (0.04) )</td>
<td>4.26b ( (0.15) )</td>
<td>4.79b</td>
</tr>
</tbody>
</table>

* Volumetric expansion coefficients measured with a dilatometer in a Perkin-Elmer TMA7 thermomechanical analyzer.

**TABLE IV**

<table>
<thead>
<tr>
<th>Model(^{b})</th>
<th>Bengal</th>
<th>Cypress</th>
<th>( P )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear model</td>
<td>Intercept, ( B_0 )</td>
<td>53.63 (1.19)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>-0.88 (0.07)</td>
<td>&lt;0.01</td>
<td>-1.08 (0.14)</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.54</td>
<td>0.38</td>
<td></td>
</tr>
<tr>
<td>RMSE</td>
<td>3.96</td>
<td>4.95</td>
<td></td>
</tr>
<tr>
<td>Sigmoid model(^{c})</td>
<td>( a )</td>
<td>47.46</td>
<td>44.43</td>
</tr>
<tr>
<td>( b )</td>
<td>0.17</td>
<td>0.39</td>
<td></td>
</tr>
<tr>
<td>( c )</td>
<td>4.43</td>
<td>8.75</td>
<td></td>
</tr>
<tr>
<td>RMSE</td>
<td>3.72</td>
<td>4.18</td>
<td></td>
</tr>
</tbody>
</table>

* Standard error of the estimate in parentheses.

\(^{b}\) If \( B_1 = \text{regression coefficient for moisture content.} \)

\(^{c}\) \( T_g = a/(1+ \exp b	imes\text{MC})^{c}.\)
The changes in the coefficients were expressed as the ratio of $\beta$ in the rubbery state to the corresponding $\beta$ in the glassy state ($\beta_{\text{rubbery}}/\beta_{\text{glassy}}$). From the $\beta$ data for both cultivars, $\beta_{\text{rubbery}}/\beta_{\text{glassy}}$ was 0.4–24.5, with a mean of 6.0. The magnitude of the differences between the $\beta$ of brown rice in the glassy state and that in the rubbery state may contribute to differential stress within a kernel during the drying process.

Development of Models for the State Diagram
A summary of the regression models relating $T_g$ to MC is shown in Table IV. The model curves for each cultivar are shown in Fig. 5. Separate linear regressions for the two cultivars tested resulted in an $R^2 = 0.54$ for Bengal and $R^2 = 0.38$ for Cypress. However, regression testing showed that cultivar did not have a significant effect on the model ($P = 0.20$). A single linear model with an intercept of 54.5 and a slope of −0.94 described the relationship between $T_g$ and MC for both Bengal and Cypress. However, the $R^2$ was only 0.46.

The predicted $T_g$ of samples at high MC (>19%) were higher than the measured values for all the models developed. All the models accounted for the effect of only one factor, water, on $T_g$. Another factor that may have had a significant effect on $T_g$ is the molecular weight (MW) distribution of the starch. The direct relationship of $T_g$ to MW is well established; an increase in MW will typically correlate with increased $T_g$ (Slade and Levine 1991a). As an example, at ≈12% MC, reported $T_g$ of maltose, maltotriose and wheat starch are −2.5, 10.8, and 66.8°C, respectively (Zelesnak and Hoseney 1987, Orford et al 1989, Rahman 1995), showing that as sample MW increases, $T_g$ also increases. Rice harvested at higher MC levels usually contains immature kernels. The average MW of the starch in these kernels may be lower because starch synthesis may not be complete. Lower MW molecules or oligosaccharides present in immature kernels can act as plasticizers (Slade and Levine 1995) and would, therefore, be expected to lower the $T_g$ of the kernels.

Brown Rice State Diagram and Rice Drying
The linear model, based on the combined data for Bengal and Cypress, was adequate in describing the relationship of $T_g$ to MC, within the MC range that is relevant to rice drying. This model was used to illustrate how a hypothetical rice-drying process might be mapped on a state diagram (Fig. 6) (Slade and Levine 1991a). At a typical harvest sample MC of 20%, many of the kernels could be glassy because the mean $T_g$ of 36°C would be above typical field temperatures (25–30°C). During typical rice drying, the kernel temperature increases, and depending on the drying air temperature, the kernel or regions within the kernel could be either glassy or rubbery, depending on the region’s respective $T_g$. As indicated earlier and shown by the state diagram, the kernel $T_g$ would increase as the MC decreases during drying. After drying to a target MC and cooling, the kernel would again go through a glass transition and become glassy as the kernel temperature decreased.

The results obtained from measuring the thermal properties of individual brown rice kernels may be applicable to understanding the mechanism of rice kernel fissuring. The MC gradient existing within a kernel during drying could produce regions within the kernel with varying $T_g$ (Slade and Levine 1991a). Depending on the temperature, the whole kernel could be completely glassy, completely rubbery, or partially glassy and partially rubbery. The $\beta$ in the glassy and rubbery regions within the kernel are different. If the MC gradient was high, the differences in $T_g$ and in the
corresponding $\beta$ would be high. This condition would generate stress within the kernel. This stress, if greater than the kernel yield limit, could cause the kernel to fissure.

Rice kernel fissuring is affected by cultivar, harvest moisture content, and drying conditions (Chen et al 1997). The effects of these factors on kernel fissures, head rice yield, and thermal properties ($T_g$ and $\beta$) of brown rice, and a hypothesis for rice fissure formation, will be the subject of a subsequent report.

CONCLUSIONS

The $T_g$ of individual kernels of Bengal and Cypress brown rice at different MC levels were measured using DSC, TMA, and DMA. Multiple transitions were observed during DSC, with the transition occurring at 16–57°C correlating with MC. The $T_g$ observed with DSC, TMA, and DMA were comparable. The TMA method of measuring $T_g$ was applied using our laboratory-prepared Al$_2$O$_3$ and a heating rate of 5°C/min. The TMA-measured $T_g$ were used to generate state diagrams for both cultivars. The $T_g$ increased as MC decreased. The brown rice kernel $\beta$ values in the glassy region were much lower (mean $\beta$ for both cultivars = $0.87 \times 10^{-4}$°C) than the $\beta$ in the rubbery region (mean $\beta$ for both cultivars = $4.6 \times 10^{-4}$°C). Mapping a hypothetical drying process on the brown rice state diagram, and realizing the differences in thermal and hygroscopic properties within a kernel relative to the glass transition region, may help us better understand the mechanism of rice fissure formation.

LITERATURE CITED


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