Glassy State Transition and Rice Drying: Development of a Brown Rice State Diagram[1]

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 (Achanta 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 $T_g \approx 55°C$. 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 (β) 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 for EMC levels of 5, 7, and 9%, respectively. EMC were calculated using Chung'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 ($T_m = 156.6°C$ and $\Delta H = 28$ 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 pre-weighed 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 (Al_2O_3), 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 (β_{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 β measurements were observed during preliminary TMA experiments. The effect of Al_2O_3 used in the dilatometer and of the TMA heating rate on T_g and β of individual brown rice kernels for both cultivars at 20–22% MC was tested. Measurements using the Al_2O_3 included in the dilatometer kit (Perkin-Elmer No. 419-0197) were compared with Al_2O_3 prepared in the laboratory by mixing five parts of Al_2O_3 (A591-500, Lot 972444, Fisher Scientific, Hampton, NH) with one part of mineral oil (400-5, Lot 0478H6080, Sigma Chemical Co., St. Louis, MO)

(Biliaderis et al 1986). At least 36 measurements using Bengal were done for each type of Al_2O_3. With the use of the Al_2O_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 β measurements. Pearson product-moment correlations between DSC-measured T_g and MC were analyzed. Results with $P \le 0.05$ 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°C. Multiple transitions were found in almost all of the thermograms for Bengal and Cypress at MC levels ranging
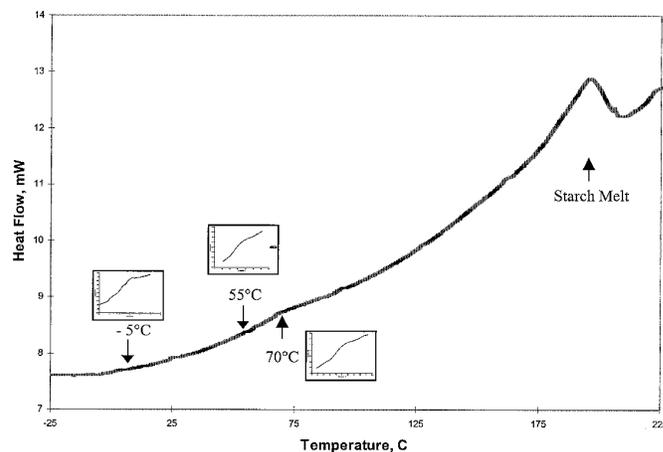
Fig. 2. Differential scanning calorimetry (DSC) thermogram of Bengal brown rice at 12% MC. Multiple transitions (slope change in heat capacity) at different temperatures indicated by arrows.
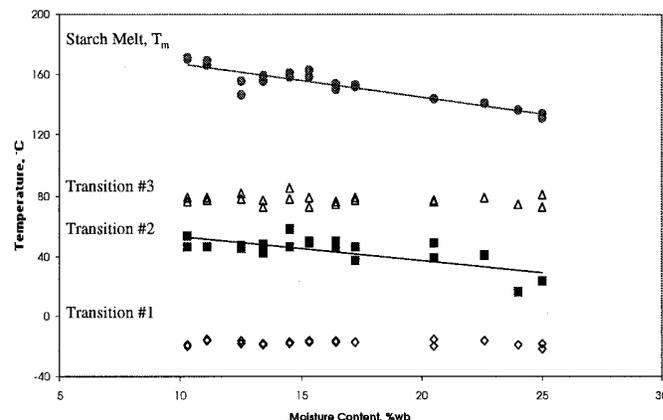
Fig. 3. Thermal transitions determined from differential scanning calorimetry (DSC) of Bengal brown rice kernels at different MC.

TABLE I
Proximate Composition and Mean Kernel Dimensions[a] of Bengal and Cypress Brown Rice Harvested in 1997[b]

Cultivar	Starch (% db)	Amylose (% db)	Protein (% db)	Length (mm)	Width (mm)	Thickness (mm)
Bengal	60.30a	20.93a	8.61a	6.2a	2.5a	1.9a
	(0.92)	(0.56)	(0.53)	(0.3)	(0.2)	(0.1)
Cypress	59.13a	28.70b	9.95b	6.8b	2.2b	1.8b
	(1.97)	(0.94)	(0.52)	(0.4)	(0.1)	(0.1)

[a] Bengal $n = 70$; Cypress $n = 88$.
[b] Values followed by the same letter in the same column are not significantly different ($P < 0.05$). Standard error of the mean in parentheses.
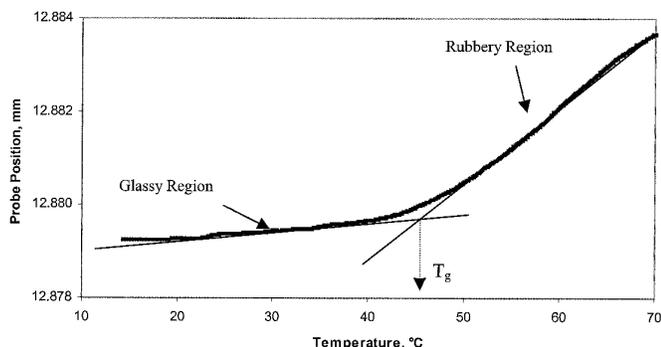
Fig. 1. Typical thermomechanical analysis (TMA) thermogram indicating assignment of glass transition temperature (T_g) and glassy and rubbery regions.

from 10 to 25%. Biliaderis (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 conformations 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 transitions occurring around –5 and 70°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°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 ≈50°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 Al_2O_3 and heating rate that gave the lowest variability in T_g and β of samples harvested at >20% MC. Analysis of variance showed that the type of Al_2O_3 used did not have a significant effect on T_g, $β_{glassy}$, and $β_{rubbery}$ ($P = 0.10$, 0.66, and 0.91, respectively). However, examination of the T_g and β measurements showed that the Al_2O_3 prepared in our laboratory resulted in lower standard errors than the Al_2O_3 from Perkin-Elmer (Table II). In addition, the mean kernel moisture loss was lower for the Al_2O_3 prepared in our laboratory, 0.6 percentage points compared with 1.6 percentage points for Al_2O_3 from Perkin-Elmer. The finer particle size of the laboratory-prepared Al_2O_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 β measurements.

The effect of three heating rates (2, 5, and 10°C/min) on T_g and β of rice kernels harvested at >20% MC was tested. Heating rate affected the measurement of T_g ($P < 0.01$) but not β ($P = 0.81$ and 0.50 for $β_{glassy}$ and $β_{rubbery}$, respectively). The mean T_g at a heating rate of 2°C/min was 28.9°C and was not significantly different from 28.1°C, the mean T_g at 5°C/min. However, both of these values were significantly lower than 34.8°C, the mean T_g obtained at the 10°C/min heating rate. This difference (which was greater 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°C/min heating rate and the laboratory-prepared Al_2O_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°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°C ($n = 6$). This was comparable to the temperature range over which the kernels showed increases in β 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 β, as measured with TMA, for individual kernels of both cultivars undergoing glass transition are shown in Table III. The mean $β_{rubbery}$ was 4.6×10^{-4}/°C, which is within the range of brown rice cubical thermal expansion coefficients reported by Arora et al (1972) and Muthukumarappan et al (1992), 3.4×10^{-4}/°C and 5×10^{-4}/°C, respectively.

TABLE II
Comparison of Standard Errors in Measuring Glass Transition Temperature (T_g) and Volumetric Expansion Coefficients (β) of Individual Brown Rice Kernels[a]

Al_2O_3	T_g (°C)	$β_{glassy}$ ($\times 10^{-4}$/°C)	$β_{rubbery}$ ($\times 10^{-4}$/°C)
Perkin-Elmer ($n = 43$)	0.81	0.07	0.32
Laboratory prepared ($n = 35$)	0.51	0.05	0.15

[a] Using different aluminum oxide types.

TABLE III
Mean Thermal Volumetric Expansion Coefficients (β)[a,b] for Individual Brown Rice in Glassy ($β_{glassy}$) and Rubbery ($β_{rubbery}$) Regions

Cultivar	$β_{glassy}$ ($\times 10^{-4}$/°C)	$β_{rubbery}$ ($\times 10^{-4}$/°C)	$β_{rubbery}/β_{glassy}$
Bengal ($n = 120$)	0.86a (0.04)	4.99a (0.17)	5.80a
Cypress ($n = 100$)	0.89a (0.04)	4.26b (0.15)	4.79b

[a] Volumetric expansion coefficients measured with a dilatometer in a Perkin-Elmer TMA7 thermomechanical analyzer.
[b] Values followed by the same letter in the same column are not significantly different ($P < 0.05$). Standard error of the mean in parentheses.

TABLE IV
Regression Models Relating Glass Transition Temperature (T_g) to Moisture Content of Individual Brown Rice Kernels[a]

Model[b]	Bengal	P	Cypress	P
Linear model				
Intercept, B_0	53.63 (1.19)	<0.01	56.27 (2.00)	<0.01
B_1	–0.88 (0.07)	<0.01	–1.08 (0.14)	<0.01
R^2	0.54		0.38	
RMSE	3.96		4.95	
Sigmoid model[c]				
a	47.46		44.43	
b	0.17		0.39	
c	4.43		8.75	
RMSE	3.72		4.18	

[a] Standard error of the estimate in parentheses.
[b] B_1 = regression coefficient for moisture content.
[c] $T_g = a/(1 + \exp^{(b \times MC) - c})$.

The changes in the coefficients were expressed as the ratio of β in the rubbery state to the corresponding β in the glassy state ($\beta_{rubbery}/\beta_{glassy}$). From the β data for both cultivars, $\beta_{rubbery}/\beta_{glassy}$ was 0.4–24.5, with a mean of 6.0. The magnitude of the differences between the β 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 m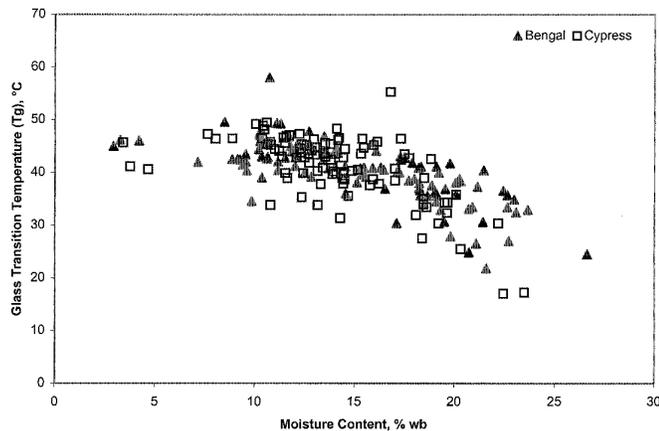odel ($P = 0.20$). A single linear model with an intercept of 54.5 and a slope of –0.94 described the relationship between T_g and MC for both Bengal and Cypress. However, the R^2 was only 0.46.

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 β 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

Fig. 4. Glass transition temperatures measured with thermomechanical analysis (TMA) of individual brown rice kernels of Bengal and Cypress, plotted against corresponding MC.
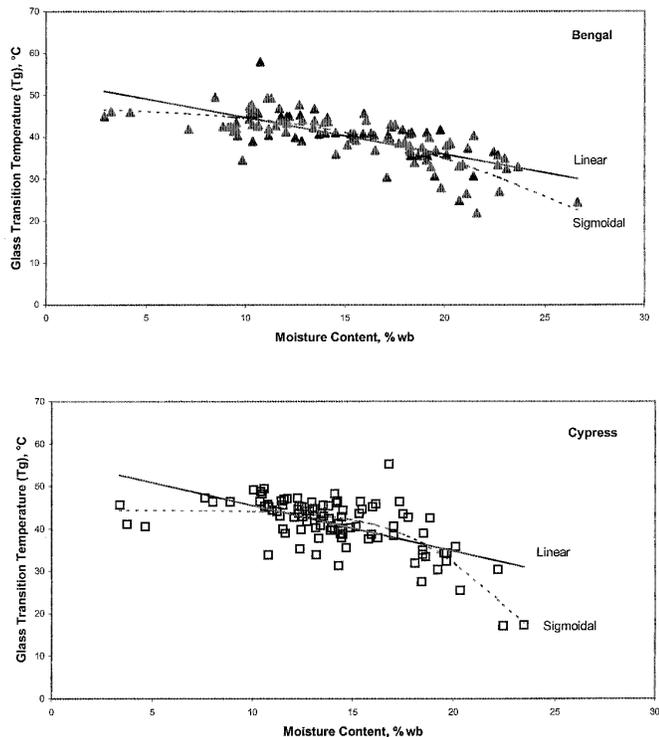
Fig. 5. Linear and sigmoidal models (see Table IV) for Bengal and Cypress brown rice state diagrams.
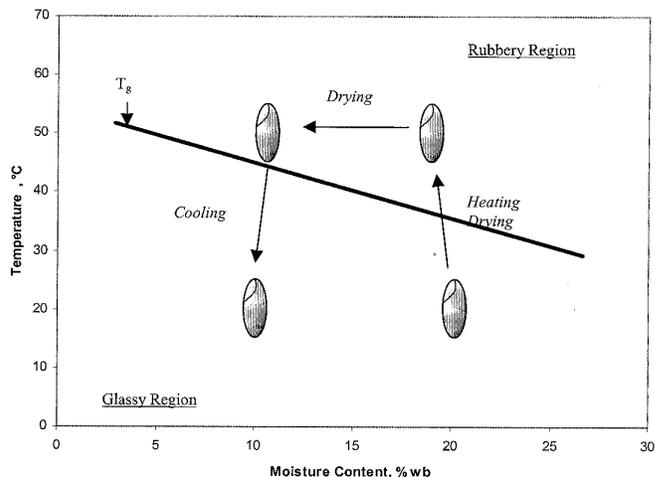
Fig. 6. Brown rice state diagram (Bengal and Cypress data combined) and a hypothetical drying process for a rice kernel.

corresponding β 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 β) 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_2O_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 β values in the glassy region were much lower (mean β for both cultivars = $0.87 \times 10^{-4}/°C$) than the β in the rubbery region (mean β 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.

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