Thermomechanical Transitions of Rice Kernels

Zhenhua Sun,[1] Wade Yang,[1] Terry Siebenmorgen,[1,2] Annemieke Stelwagen,[3] and Auke Cnossen[1]

ABSTRACT

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Thermomechanical analysis (TMA) and differential scanning calorimetry (DSC) were used to investigate the thermal transitions of long-grain rice kernels. Three distinct thermomechanical transitions were identified as rice kernels were heated from 0 to 200°C. The identified transitions were a low temperature transition with onset at ≈45°C, an intermediate temperature transition at ≈80°C, and a high temperature transition at ≈180°C. Low temperature transition with onset from ≈60°C at 5% moisture content (MC) to 30°C at 20% MC was identified as the glass transition of the rice kernels. Intermediate temperature transition from 60 to 100°C, depending on MC, may be caused by rapid evaporation of moisture in the rice kernels. High temperature transition was associated with melting of the crystalline structure of rice starch. The temperatures of all three transitions decreased as MC increased, confirming that moisture acted as a plasticizer in rice kernels.

Rice is normally harvested at 16–22% moisure content (MC, expressed on a wet basis unless otherwise specified) and must be dried to ≈13% MC for safe storage. Severe drying conditions can increase the number of fissured kernels (Kunze and Prasad 1978; Kunze 1979; Sharma and Kunze 1982; Cnossen and Siebenmorgen 2000; Fan et al 2000). Because fissured kernels considerably lower the market value of milled rice, an effective drying process is required to produce optimal head rice yield. Recent research (Perdon 1999; Perdon et al 2000) suggested that thermomechanical properties of rice kernels such as the glass transition temperature (T_g) are important to rice drying and fissuring behavior. However, with the current knowledge of grain drying, it is not entirely clear how T_g and other transitions affect the drying process of rice. A study of thermomechanical properties of rice kernels may provide pertinent information.

A rice kernel can be regarded as a composite consisting of several different biopolymers, including starch (mixture of amylose and amylopectin) and proteins with moisture as a plasticizer. It is therefore possible for multiple thermomechanical transitions, which are closely related to the structure and morphology of rice kernels, to occur during processes involving heating. Information on these transitions could help understand the structure-property relationship of rice kernels, thereby helping to develop a more effective drying process.

Thermomechanical transition properties of polymeric materials can be studied by several techniques: differential scanning calorimetry (DSC) (Brandrup and Immergut 1975), dynamic mechanical analysis (Ferry 1980), dielectric spectroscopy (Boyer 1966), thermally stimulated current (Brandrup and Immergut 1975), high-resolution nuclear magnetic resonance (NMR), and thermomechanical analysis (TMA) (Rabek 1980). The T_g and gelatinization behavior of starch-water systems has been studied by many researchers using various methods. The most widely used method for this application is DSC. However, most studies focused on systems of starch in excess water (Stevens and Elton 1971; Slade 1984; Biliaderis et al 1986; Yost and Hoseney 1986; Slade and Levine 1987, 1991; Liu and Lelievre 1991; Marshall and Normand 1991; Huang et al 1994; Buera et al 1998). Only a few studies were conducted on starch-water systems with a low moisture content (Slade 1984; Slade and Levine 1987, 1991; Zeleznak and Hoseney 1987; Liu and Lelievre 1991; Kalichevsky et al 1992; Perdon 2000). Slade (1984), Zeleznak and Hoseney (1987), and Slade and Levine (1987, 1991) showed that T_g of wheat starch is extremely sensitive to moisture content. When moisture content was reduced from ≈20 to 7%, T_g of wheat starch increased from 30 to 125°C. The T_g of amylopectin also showed a similar trend (Zeleznak and Hoseney 1987). However, generally, the sensitivity of DSC is low because polymers with a relatively high crystalline structure content have a relatively low amorphous content. Thus, the change in heat capacity at T_g becomes less conspicuous and more difficult to detect by DSC. Because a rice kernel is a partially crystalline and partially amorphous polymer composite, a single technique usually does not suffice in determining all thermomechanical transitions. This study was conducted to elucidate thermomechanical transitions in rice kernels at 0–200°C using a combination of TMA and DSC.

MATERIALS AND METHODS

Long grain rice (cv. Drew) at 21.7% harvest MC was harvested from the University of Arkansas Rice Research and Extension Center at Stuttgart, AR, in 1999. Immediately after harvest, the rice was cleaned with a dockage tester (Carter-Day Co., Minneapolis, MN) and divided into different lots. Each rough rice lot was dried in a thin layer to different moisture content levels. Drying conditions were controlled at 40°C and 17% rh (Climate-Lab-AA, Parameter Generation & Control Inc., Black Mountain, NC) in chambers to produce samples with 7.6–21.7% MC. A rice sample with ≈5% bulk MC was obtained by further drying the rice at 7.6% MC in a dessicator containing anhydrous calcium sulfate. The samples were placed in sealed plastic bags and stored at 4°C for at least 24 hr to equilibrate moisture before further analysis. The moisture content of each rice sample was analyzed by drying duplicate subsamples for 24 hr in an oven at 130°C (Jindal and Siebenmorgen 1987).

The temperature transitions of the brown rice kernels were measured with a thermomechanical analyzer (Perkin-Elmer, TMA7) and a differential scanning calorimeter (Perkin-Elmer, Pyris 1). For TMA analysis, individual kernels were randomly sampled in duplicate from each dried rough rice sample and dehulled by hand (76 kernels in the entire moisture content range). The T_g measurement followed a procedure similar to that reported by Perdon et al (2000). In brief, the mass of a brown rice kernel was measured with an analytical balance. The kernel was then placed in a quartz dilatometer (7.1 mm, i.d.). The dilatometer was filled with pure aluminum oxide powder (Al_2O_3) and covered. Then it was placed in the sample holder of the TMA and a displacement probe was used to detect the displacement caused by the volume change of the sample during heating. The sample was held isothermally at 4°C for 5 min, and then heated from 4 to 200°C at a rate of 5°C/min. Software (Perkin-Elmer thermal analysis software v. 4.00) was used to determine the temperatures at the different transitions of rice kernels. After TMA measurement, the kernel was reweighed to calculate moisture loss. The moisture content was subsequently analyzed by drying the kernel for 24 hr in an oven set at 130°C.

To determine the temperature transitions of rice starch, the dilatometer was filled with rice starch (food grade, 10.4% MC, provided

[1] Department of Food Science, University of Arkansas, 2650 N. Young Ave., Fayetteville, AR 72704.
[2] Corresponding author. E-mail: tsiebenm@uark.edu Phone: 501-575-2841. Fax: 501-575-6936.
[3] Department of Food Sciences, Wageningen University, The Netherlands.

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by Riceland Foods, Stuttgart, AR) and covered. The rice starch in the cell was compressed into a compact cylinder by pressing the cover down manually. The TMA procedure above was followed.

The melt temperature (T_m) of rice kernels was measured using the Pyris 1 differential scanning calorimeter equipped with an Intracooler II (Perkin-Elmer). The calorimeter was calibrated with indium (T_m = 156.6°C and ΔH = 28 J/g). Six rough rice kernels per moisture content level were dehulled by hand and the brown rice kernels were coarsely ground in a mortar. Samples (≈5 mg of ground rice) were placed in a preweighed high-pressure stainless steel pan (Perkin-Elmer) and sealed. A sealed, empty high-pressure stainless steel pan was used as a reference. The sample was placed in the sample holder of the calorimeter, held isothermally at 4°C for 5 min, and then heated from 4 to 200°C at a rate of 5°C/min. Thermal analysis software (Perkin-Elmer v. 1.0.0) was used to determine T_m and calculate ΔH_m.

The T_g of rice cv. Drew in this study was statistically compared with those of rice cvs. Bengal and Cypress as reported by Perdon (1999) and Perdon et al (2000). Since a linear relationship between T_g and MC was assumed to be in the MC range typical of rice drying (≈12–22%), the statistical analysis involved testing whether the regression lines of T_g values of Drew and the combined T_g values of Bengal and Cypress had the same slope and intercept. Linear regression with indicator variables (Neter et al 1985) were:

$$T_g = b_0 + b_1 \bullet \mathrm{MC} + b_2 \bullet X + b_3 \bullet \mathrm{MC} \bullet X \quad (1)$$

where b_0 to b_3 are regression constants, and X is an indicator variable that assumes 1 if T_g was obtained in this study and 0 if otherwise. The regression was determined using SAS. The statistical test involves the statements for H_0 ($b_2 = b_3 = 0$) and H_a (not both $b_2 = 0$ and $b_3 = 0$). If the calculated t statistic is smaller than the tabulated value at a given confidence level, then H_0 is concluded. Otherwise, H_a is concluded.

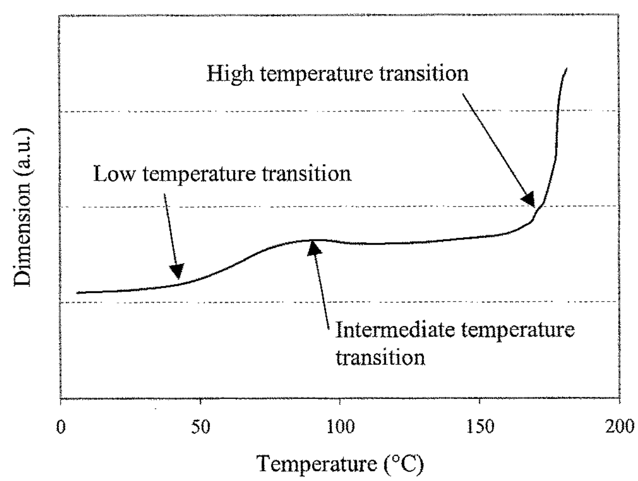

Fig. 1. Thermomechanical analysis curve for a brown rice kernel (cv. Drew, 14.4% moisture content). On the *y* axis, a.u. stands for arbitrary unit.

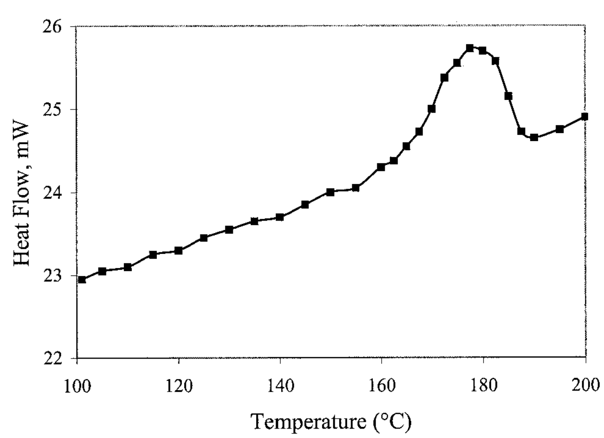

Fig. 2. Differential scanning calorimetry thermogram at 100–200°C for coarsely ground brown rice kernels (cv. Drew, 14% moisure content).

RESULTS AND DISCUSSION

Low, Intermediate, and High Temperature Transitions

The TMA curve of a brown rice kernel at 14.4% MC (Fig. 1) shows three transitions at >0°C: a low temperature transition with onset at ≈45°C, an intermediate temperature transition at ≈90°C, and a high temperature transition at ≈180°C. Although brown rice kernels at all moisture content levels showed the three transitions, their corresponding transition temperatures changed with moisture content.

The low temperature transition was taken to be the T_g of rice kernels. Perdon (1999) and Perdon et al (2000) conducted similar TMA tests and found that the thermal expansion coefficient of rice kernels, which characterizes T_g, increased substantially for rice kernels at the low temperature transition. Statistical tests substantiated that the low temperature transition was the T_g of the rice kernels.

In addition to the low temperature transition, an intermediate and high temperature transition were also detected with TMA. Based on the magnitude of temperatures at these transitions, the high temperature transition may be due to the melting of the crystalline structure in the rice starch. DSC results were used to confirm our conjecture. The DSC thermogram for ground brown rice at 100–200°C is shown in Fig. 2. The melting peak of the crystalline structure of the rice starch is shown at ≈180°C. This melting temperature (T_m), measured by DSC, corresponded to the high temperature transitions detected by TMA.

Moisture Dependence of the High Temperature Transition

The moisture content dependence of T_m and melting enthalpy (ΔH_m) of brown rice kernels determined using DSC are shown in Figs. 3 and 4, respectively. The data in Fig. 3 indicate that T_m

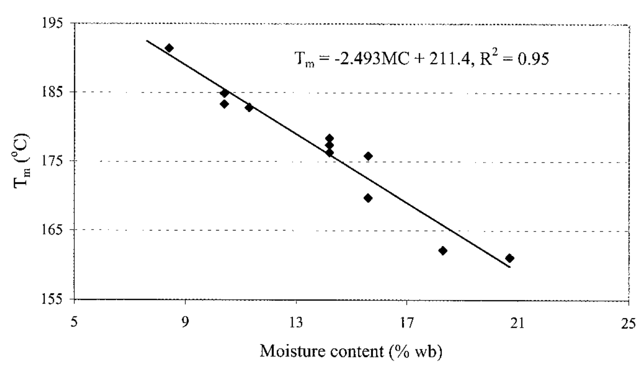

Fig. 3. Melting temperature (T_m) of coarsely ground brown rice kernels (cv. Drew) as a function of moisture content.

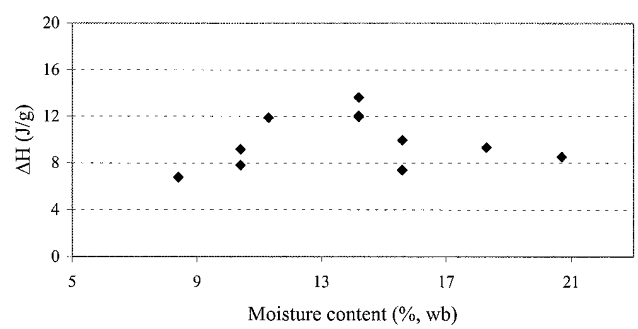

Fig. 4. Melting enthalpy (ΔH) of coarsely ground brown rice kernels (cv. Drew) in relation to moisture content.

decreased linearly with increasing moisture content, which suggested that moisture could cause increasing imperfection in the crystalline structure of rice kernels at high temperatures (Slade and Levine 1987). No clear relationship was found between ΔH_m and MC (Fig. 4).

Contribution of Starch to T_g of Rice

To understand the mechanism and moisture content dependence of the low and intermediate temperature transitions, TMA curves for brown rice kernels at three mositure contents tested from 10°C to ≈150°C are shown in Fig. 5. A brown rice kernel is primarily a mixture of starch and protein with a small quantity of lipids. It is not clear whether the low temperature transition in Fig. 5 is due to the T_g of rice starch or rice protein. The results of the TMA tests on pure rice starch were used to address this question. Figure 6 shows the resultant TMA curve from such a test with rice starch at 10.4% MC. Rice starch underwent a distinct transition at an onset temperature ≈42°C at this moisture content. This transition temperature of rice starch was very close to that of the low temperature transition shown by rice kernels at a similar MC levels (Figs. 1 and 5). These results suggest that rice starch may have been the primary contributor to the low temperature T_g of rice kernels.

Comparison of T_g Values

The T_g of Drew measured in this study compared favorably with that of Bengal (medium grain) and Cypress (long grain) reported by Perdon (1999) and Perdon et al (2000) (Fig. 7). By visual inspection, these two sets of data appear similar, except in the lower moisture content range where T_g values measured by Perdon et al (2000) were slightly lower than those obtained in this study. Statistical tests, by means of indicator variables for comparison of two regression functions (Neter et al 1985), were conducted to examine whether the two sets of T_g data were different. The two data sets, approximated by a linear relationship between T_g and MC, were not significantly different ($\alpha = 0.01$) from each other. The T_g of rice kernels decreased with increasing moisture content. In the moisture content range shown in Fig. 7, the T_g vs. MC relationship for this study could be approximated by a linear function as:

$$T_g = 59.47 - 1.17\ \text{MC},\ R^2 = 0.57 \quad (2)$$

For the combined data, the relationship was:

$$T_g = 57.03 - 1.08\ \text{MC},\ R^2 = 0.53 \quad (3)$$

where MC is in % wb.

Thermomechanical Intermediate Transition Due to Rapid Moisture Evaporation

When the moisture content was high, the rice kernel shrank when the temperature exceeded T_g (Fig. 5, middle and top curves). The shrinkage of the rice kernels could be due to crystallization, to the evaporation of moisture, or to structural collapse above T_g (Slade and Levine 1991; Cheng et al 2000). In this study, no crystallization was seen in any of the DSC runs conducted and no visual kernel shape distortion was observed to suggest that there was structural collapse of rice kernels during TMA tests. Instead, reasoning

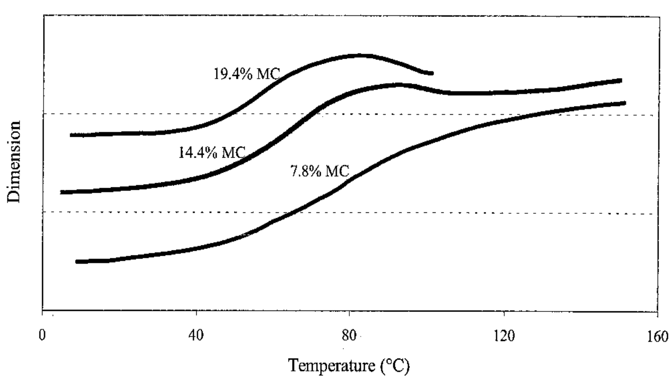

Fig. 5. Thermomechanical analysis curves for brown rice kernels (cv. Drew) at different moisture contents. Distance between two dashed lines on the *y* axis is 0.01 mm.

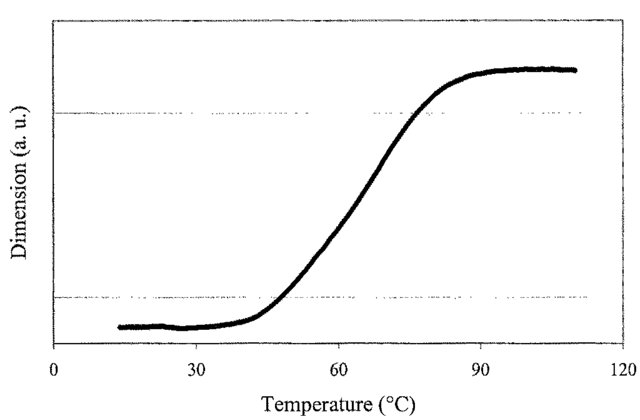

Fig. 6. Thermomechanical analysis curve for rice starch at 10.4% moisture content.

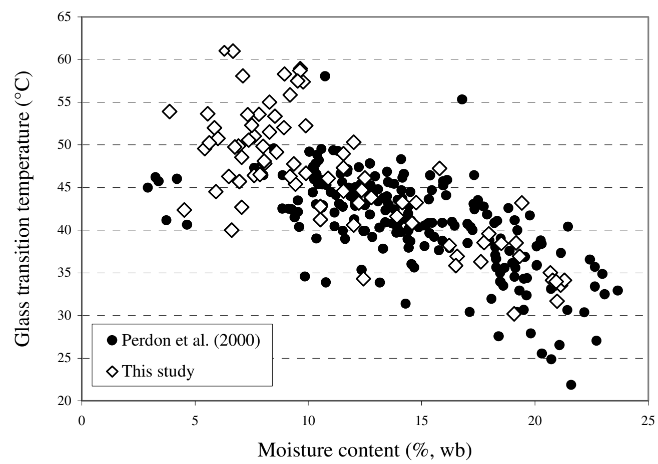

Fig. 7. Glass transition temperature vs. moisture content for brown rice kernels (cv. Drew in this study; cvs. Bengal and Cypress in Perdon et al [2000]).

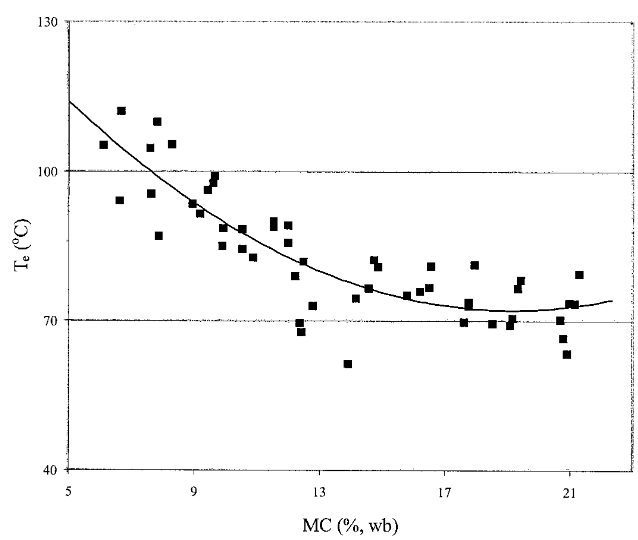

Fig. 8. Rapid evaporation temperature (T_e) as a function of moisture content for brown rice kernels (cv. Drew).

suggests that the intermediate temperature transition was the result of a rapid evaporation of moisture. Even though Al_2O_3 powder was used to cover brown rice kernels to prevent moisture loss during TMA tests, moisture loss still occurred when a rice kernel at high moisture content was heated above T_g. A rice kernel with 18.3% MC dropped to 15.2% when the rice kernel was heated from 4 to 100°C, however, the moisture loss of a rice kernel at 7.6% MC was negligible when it was heated from 4 to 150°C in TMA tests. Because volume and dimension reduction of rice kernels is common during dehydration (Kramer 1951; Wratten et al 1969; Morita and Singh 1979; Steffe and Singh 1980; Muthukumarappan et al 1992; Sun et al, *unpublished*), it may be that when the moisture content was high, the shrinkage of rice kernels during heating with resultant moisture loss was quite large; but when moisture content was very low, the transition almost disappeared (Fig. 5, bottom curve).

The effect of moisture content on intermediate transition temperature, which will be referred to as the rapid moisture evaporation temperature (T_e), is shown in Fig. 8. The T_e decreased with increasing moisture content. To describe this relationship, quadratic, exponential, logarithmic, and power equations were tested. The best fit was produced by the quadratic function:

$$T_e = 0.21\text{MC}^2 - 8.02\text{MC} + 149, R^2 = 0.74 \quad (4)$$

Application to Drying Processes

The melting temperature of rice starch plays little role in rice drying because drying temperatures usually do not reach the magnitude of the melting temperature, but the T_g of rice kernels can be very important in rice drying. The T_g will significantly affect the drying rate, fissuring, and tempering of rice kernels. If the drying temperature is below T_g, the rice starch exists in a glassy solid state, the rice starch granule is compact, and the water associated with the starch is relatively immobile (Slade and Levine 1991). Therefore, the diffusion of moisture inside the rice kernel would be very slow, and it would take a longer time to dry rice kernels to a targeted moisture content. If the drying temperature were above T_g, the rice starch would exist in the rubbery state, rice starch macromolecules would have greater free volume, and the starch would be more mobile (Slade and Levine 1991). Moisture could thus diffuse out of rice kernels much faster. To this end, the minimum drying air temperature for an effective drying process should, theoretically speaking, be higher than T_g. However, the faster the moisture removal, the greater the moisture gradient created because the surface dries quicker than the inner part of the kernel. Moisture gradient differences within the rice kernel produce stress that can cause the kernel to fissure when it exceeds the tensile strength of the rice kernel under no tempering (Bautista et al 2000). Meanwhile, Cnossen and Siebenmorgen (2000) found that tempering of rice kernels after a drying pass was required to maintain high head rice yields if drying temperature was above T_g and if sufficient moisture content gradients in kernels existed. Cnossen and Siebenmorgen (2000) concluded that drying air temperatures as high as 60°C can be used without reducing head rice yields as long as sufficient tempering at a temperature above T_g was employed.

SUMMARY AND CONCLUSIONS

Data collected using TMA and DSC indicated that rice kernels experienced three thermomechanical transitions between 0 and 200°C: a low temperature transition, an intermediate temperature transition, and a high temperature transition. The low temperature transition was taken to be the T_g of rice kernels. The intermediate temperature transition was suggested to be related to rapid evaporation of moisture in the rice kernels. The high temperature transition was related to the melting of crystalline starch. All three transitions were inversely related to kernel moisture content. The T_g of rice determined in this study was not significantly different from that reported by Perdon et al (2000).

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