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Investigation of Fissure Formation During the Drying and Post-Drying of Japonica Aromatic Rice

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ABSTRACT

Fissure formation Mechanism of Kaori aromatic rice under different drying and post-drying conditions was investigated by differential scanning calorimetry (DSC). Samples dried at 50°C and 60°C to standard and low final moisture content (FMC), the maximum fissuring rate occurred after approximately 12 h. Increasing difference between storage and drying air temperatures increased fissured kernels. The mean value of glass transition temperatures (Tg) showed that to achieve a FMC up to 12% and 9%, the temperature must be below 45°C and 52°C, respectively. Drying temperatures higher than these are likely to produce a high proportion of fissured kernels. The DSC diagram indicated that at the onset of drying, kernels state changed from a glassy to a rubbery and during the drying it returned to the glassy state. Therefore fissured kernels at low FMC was approximately 10% more than standard FMC. It can be concluded that a high drying temperature might have a more negative effect than low FMC on the structure of Kaori aromatic rice and leads to deterioration in its quality.

Key Words: Drying; Differential scanning calorimetry; Fissure; Glass transition temperature

INTRODUCTION

Flat-bed dryers, which are widely used in Iran, use constant procedures to remove moisture content (MC) from freshly harvested rice. Non-uniformity in MC and over-drying of grains, which subsequently cause a low final moisture content (FMC) of grains at less than 9%, often occurs in batch dryers (Hashemi *et al*., 2005). Improper drying processes and post-drying conditions can be a major cause of fissuring (Ban, 1971; Kunze & Choudhury, 1972; Kunze, 1979; Sharma & Kunze, 1982). The magnitude of fissuring is dependent on the thickness of the kernel, the FMC and the conditions in which samples are dried. Several researchers (Ban, 1971; Kunze, 1979; Sharma & Kunze, 1982; Li *et al*., 1999; Qingling *et al*., 2003; Siebenmorgen *et al*., 2005) have observed that almost of fissures occur after drying process has ceased. Sharma and Kunze (1982) stated that few whole rough rice kernels fissure during the drying process itself. It is obvious that severe drying conditions would generate extensive kernel fissuring with a significant reduction in head rice yield (HRY) (Arora *et al*., 1973; Cnossen & Siebenmorgen, 2000; Hashemi *et al*., 2006). As most kernels are not fissured immediately after drying, a small amount of research has considered post-drying fissure development in rough rice, especially in short grain rice. Sharma and Kunze (1982) reported that most fissures appear within 48 h of the cessation of drying.

The thermal properties of starch might explain fissure formation. A change in the state of starch, as it goes through a glass transition temperature (Tg), has been identified (Perdon, 1999) to play an important role in the rice drying process. Many researchers (Normand & Marshall, 1989; Biliaderis *et al*., 1993; Huang *et al*., 1994; Perdon *et al*., 2000) have performed a thermal analysis of rice starch using differential scanning calorimetry (DSC) to elucidate the gelatinization properties of starch. Perdon *et al*. (2000) reported that the physical properties of a rice kernel changed dramatically as the kernel temperature passed through Tg. Perdon *et al*. (2000) and Sun *et al*. (2002) investigated the relationship between the thermal properties of rice starch and the number of fissured kernels. They observed that fissures in rice kernels are perpendicular to the varieties of the kernel due to un-uniform shrinkage. They also found that kernels shrank un-evenly in length and thickness, with the percentage shrinkage in thickness consistently more than that in length.

There is no report on relationship between source of fissure creation and FMC, particularly at a low FMC level. However, regarding the rice drying conditions in Iran, this research is mainly concerned with understanding the fundamental mechanism of fissure creation and explaining the thermal properties of short grain aromatic rice during the drying and post-drying periods by polymer science. This research might enable us to develop processes and

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procedures to minimize losses and maintain rice quality as much as possible.

MATERIALS AND METHODS

Freshly harvested *Kaori* rice of the aromatic, short grain variety (procured from the Agriculture Research Farm of the University of Tsukuba, Japan), containing approximately 26% MC, was selected for this study. Immediately after harvest, the rice was cleaned and placed in a refrigerator at 5°C until required. Drying experiments were performed using a batch-type dryer, in same drying chamber as described by Hashemi *et al*. (2006). Three principal diameters (length, width & thickness) of brown rice were measured manually by a Micrometer having +/- 0.001 mm precision. The initial dimensions of brown rice samples were (l/w) = 1.7 as a slenderness ratio and (t) = 2.12 mm as grain thickness.

Experimental details. Experiments consisted of different drying conditions resulting from combination of drying air temperatures and different drying times corresponding to a FMC of about 12%, representative of the standard FMC for milling and safe storage (ASAE, 1982) and about 9%, representative of the low FMC widely produced in Iran (Hashemi *et al*., 2005). Based on the suggestion of Arora *et al*. (1973), a drying temperature of 50°C was considered to be optimum for rice quality. Other temperatures below and above this approved level were also tested. Hence, the experiments were carried out at four drying temperatures, namely 30, 40, 50 and 60°C, with different durations of drying time, until the FMC of paddy was reduced to about 12% or 9%.

When samples dried at each temperature had reached the desired FMC levels, one-hundred grams of each sample was randomly selected for fissure enumeration after 1, 12, 24 or 48 h for the presence of fissures in storage conditions (22°C & 50% RH). Then, samples were placed in zip-lock plastic bags for further test. These times are in accordance with the findings reported by Sharma and Kunze (1982) and Li *et al*. (1999) that there is no further increase in the number of grains with fissures beyond 48 h.

For comparison with experimental data, a reference sample was dried in a temperature- and humidity-controlled chamber (Humidity Cabinet, LHL-113, TABAI Espec Corp. Japan), which was set at 25°C, 60% RH, corresponding to a rice equilibrium MC of approximately 12.5% (Perdon *et al*., 2000). Number of fissured kernels was counted before and after drying experiments in each condition. One hundred rice kernels randomly picked from each sample were manually dehulled and each kernel was inspected using a grain scope (TX-200, Kett Electric Laboratory, Tokyo, Japan). The initial and final MCs of these rice samples were determined by drying duplicate samples for 72 h in an air-oven set at 105°C (ASAE, 1982).

Differential scanning calorimetry measurement. For every treatment, 3 g rough rice was dehusked by hand and the brown rice kernels were used. Pulverizing was performed by placing brown rice kernels in a porcelain mortar and pestle and grinding at a slow rate, during which no perceptible heat was generated (Marshall, 1992). The brown rice powders were collected and kept in sealed containers. Five mg of rice powder was placed in a pre-weighed high-pressure stainless steel pan (Perkin- Elmer), which was then sealed hermetically (Zhenhua *et al*., 2002). Before scanning, the sample was allowed to equilibrate at room temperature for about 60 min. A DSC instrument (DSC 6100, Seiko Instrument Inc., Chiba, Japan) with an EXSTARS 6000 thermal analysis processor was used to measure the Tg and Tm of rice kernels. The DSC was calibrated with indium (T_m = 156.6°C & ΔH =28 J/g). Thermograms were obtained within a temperature range of 20–220°C at a scanning rate of 3°C min^{-1}. An empty aluminum pan with the same weight was used as a reference. In all runs, the outer surfaces of the pans were flushed with nitrogen gas at a rate of 30 mL min^{-1} to prevent condensation. In general, differential heat flow is calculated by subtracting sample heat flow from reference heat flow. When following this convention, endothermic processes are negative and below baseline (Dean, 1995). The MC of rice powder was determined by drying two grams of powder sample in an oven at 135°C for one hour.

Statistical analysis. Experiments were performed in duplicate for each rice lot under each variation of temperature and FMC parameters and the mean values are reported. Analysis of variance (ANOVA) as a two-factor experiment in completely randomized design (2F-CRD) was performed at a significance level of 0.01 unless otherwise indicated (Table I). The two factors are expressed as drying temperature and FMC, with four and two levels, respectively.

The experimental variables included drying rate (dR), fissure at 1, 12, 24 and 48 h post-drying duration (F1, F12, F24, F48), first transition temperature (Tg), second transition temperature (Tg2), melting temperature (Tm). A Pearson correlation test was performed among the above variables using SPSS version 10.2 statistical software (Table II).

RESULTS AND DISCUSSION

Fissure formation. Fig. 1 shows the percentage of fissured kernels at each indicated post-drying duration in the samples dried at different drying temperatures at an FMC of about 12% (Fig. 1a) or 9% (Fig. 1b). With increasing post-drying duration, the percentage of fissured kernels significantly ($P<0.01$) increased in both standard and low FMC treatments. The magnitude of the fissured kernels was different. After one hour of drying process ceased, the percentage of fissured kernels was between 4% and 22% for grains with a standard FMC and between 2% and 30% for grains with a low FMC. For samples dried at 50°C and 60°C, the maximum percentage of fissured kernels was about 60%

Table I. Statistical data of the physical and thermal properties of Kaori aromatic rice

Variables		FMC	dR	F_1	F_{12}	F_{24}	F_{48}	Tg	Tg2	Tm
Statistical items	*df*	F_c	F_c	F_c	F_c	F_c	F_c	F_c	F_c	F_c
Drying temperature	3	1.8^{ns}	212^{**}	28^{**}	111^{**}	390^{**}	319^{**}	2.8^{ns}	3.4^{ns}	1.6^{ns}
Final MC	1	310^{**}	70.7^{**}	1.3^{ns}	14.4^{**}	53.4^{**}	52.0^{**}	7.8^{*}	0.6^{ns}	0.9^{ns}
Temperature & FMC	3	0.8^{ns}	1.9^{ns}	1.6^{ns}	2.4^{ns}	8.9^{*}	6.4^{*}	0.9^{ns}	5.7^{*}	2.9^{ns}

^{ns} Not significant, * Significant at level of 5%, **Significant at level of 1%,

Table II. Pearson's correlation of the physical and thermal properties of Kaori aromatic rice

Variables	FMC	F_1	Tg	Tg2	Tm	F_{12}	F_{24}	F_{48}
F	-0.36	--	--	--	--	--	--	
Tg	-0.77**	-0.18	--	--	--	--	--	--
Tg2	-0.48	-0.19	0.61*	--	--	--	--	--
Tm	-0.02	0.76*	-0.45	-0.45	--	--	--	--
dR	-0.08	0.89**	-0.29	-0.015	0.62	0.86**	0.86**	0.87**

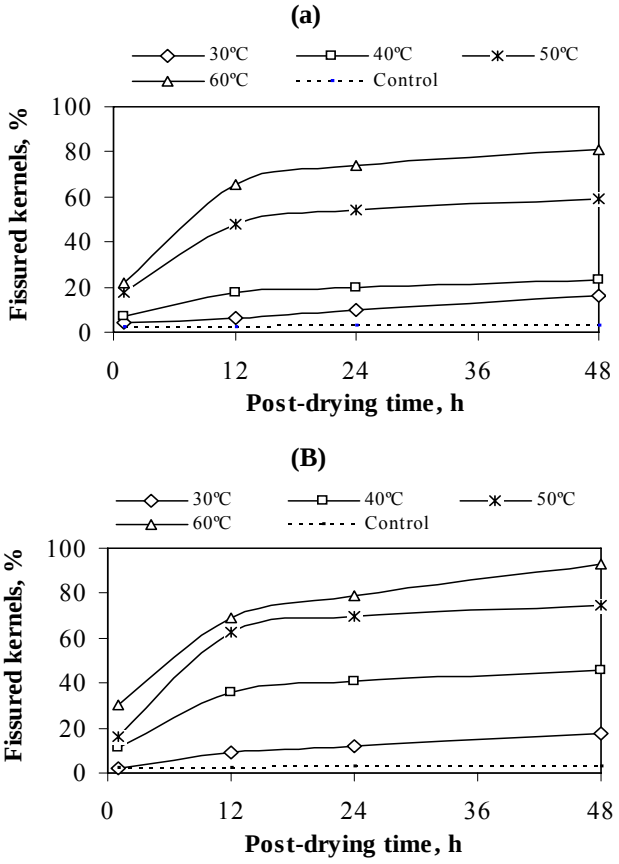
* Significant at level of 5%, **Significant at level of 1%,

and 80%, respectively for grains at a standard FMC and 75% and 96%, respectively for grains at a low FMC, after 48 h. Drying creates moisture and temperature gradients within a kernel. If the moisture gradient is sufficiently large, it causes the kernel to fissure (Kunze, 1979; Yang *et al.*, 2003; Siebenmorgen *et al*., 2005). The effect of post-drying duration on the percentage of fissured kernels (Fig. 1) could be explained by drying temperature, storage conditions, final moisture and kernel thickness.

Drying temperature. The percentage of fissured kernels increased with drying temperature at different post-drying durations. The maximum number of fissures occurred at a drying air temperature of 60°C followed by 50°C, 40°C and then 30°C, in grains of both FMCs. The final curves aligned themselves in the order of increasing fissures with increasing drying temperature and decreasing FMC. The final fissuring response following drying at 60°C was nearly 5 times as great as that following drying at 30°C, in grains of the same FMC. Statistical analyses show that drying temperature had a significant ($p<0.01$) effect on the fissure formation at different post drying durations, regardless of FMC (Table I). This confirms the finding reported by Siebmorgen *et al*. (2005) in samples dried under severe drying conditions. It is also assumed that a high drying rate will result from a high drying temperature. As indicated in Table II, the correlation between fissure formation and drying rate at 1 h (0.89), 12 h (0.86), 24 h (0.86) and 48 h (0.87) of post-drying duration was indeed significant ($P<0.01$) showing that drying temperature possibly caused an increase in the number of fissured kernels.

Storage conditions. Grains in storage absorb moisture when the FMC is less than the equilibrium moisture. This condition will cause grains to fissure within a few hours of the end of the drying process (Kunz & Prasad, 1978; Li *et al*., 1999; Yang *et al*., 2003). In this experiment, the average temperature and RH of storage were 22°C and 55%, respectively. As clear from Fig. 1, the occurrence of fissuring is less in rice dried at 30°C and 40°C, which are close to the storage temperature. This result is consistent with previous reports (Sharma & Kunz, 1982; Li *et al*., 1999; Siebmorgen *et al*., 2005), which the percentage of fissured kernels increased by increase in the difference between storage and drying temperatures.

Fig. 1. Percentage of fissured kernels during 48 h of post-drying, for samples dried at indicated drying temperature to (a) a standard FMC of about 12% and (b) a low FMC of about 9%. The control sample was dried at 25°C-60% RH



Final moisture. The percentage of fissured kernels with low FMC (Fig. 1b) was about 15% higher than that of kernels with standard FMC (Fig. 1a), at different post-drying

Fig. 2. Thermal transition of Kaori aromatic rice measured by DSC at different MC

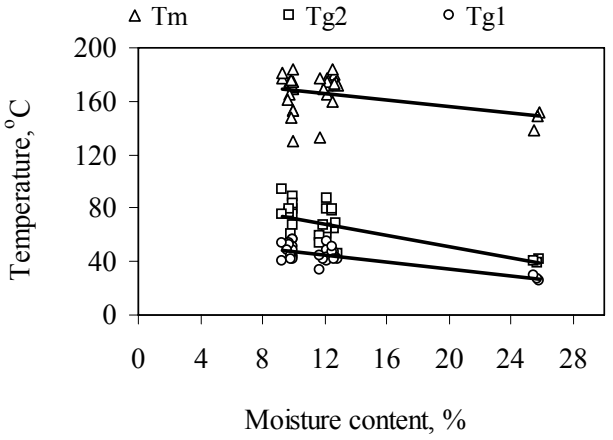
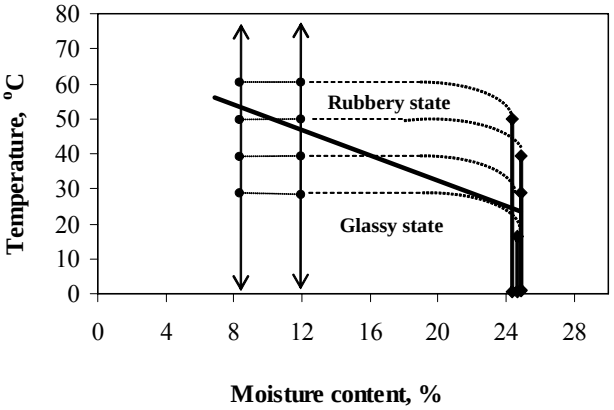


Fig. 3. Macroscopic indications of kernel states during the drying process



durations, in particular at temperatures higher than 50°C. This shows that grains with a low FMC have the potential to fissure due to the adsorption of moisture when they reach the EMC level. During the adsorption period, cells in the surface layers become swollen, producing compressive stresses that are balanced by tensile stresses in the inner portion of the kernel (Kunze & Choudhury, 1972). If the resulting tensile stresses exceed the tensile strength of the central portion of the kernel, fissuring occurs.

The visual appearance of fissures occurred almost entirely within 12 h of cessation of drying, then reaching a steady state; the appearance of fissures was completed by 48 h. A similar fissure-producing trend was reported by Siebmorgen *et al*. (2005), stating that all fissures occur within 24 h after drying, regardless of the drying temperature and variety and are completely formed by 48 h. Therefore, this finding supports the earlier statement that the difference between drying temperature and post-drying temperature is more critical within 12 h of the cessation of the drying process. Statistical analyses revealed that FMC has a significant (P<0.01) effect on the number of fissured kernels after the completion of a 12 h drying process. This is because of moisture adsorption effects, which occur after 12 h. The obtained results are consistent with those described above.

Thickness. As mentioned earlier, the maximum percentage of fissured kernels was about 80% and 93% for grains of standard and low FMC, respectively in Kaori aromatic rice. The amount of fissured kernels found in this study was higher than that reported by Siebenmorgen *et al*. (2005) but similar to that reported by Sharma and Kunze (1982). A comparison of their results and our own revealed that the thickness of kernels might contribute to the difference in the percentage of fissured kernels via an increasing moisture gradient. The average thickness of the Kaori variety was 2.12 mm, which is about 35% more than that of the variety used by Siebenmorgen *et al*. (2005) and almost same as that of the medium grain variety used by Sharma and Kunze (1982). It is clear that thicker kernels are more susceptible to fissuring than thin kernels due to the large moisture gradient, particularly after severe drying conditions (Jindal & Siebenmorgen, 1994). As the moisture gradient decreases gradually after drying, moisture from the central portion of the grain diffuses to the surface causing the surface to expand, while the internal portion contracts due to the loss of moisture.

Increase in the number of fissured kernels at higher drying temperatures is related to the severe drying condition, which subsequently increased the fissured kernel regardless of FMC. Under severe drying conditions, temperature has a greater effect on the percentage of fissured kernels than FMC. However, at low drying temperatures, the effect of temperature on the percentage of fissured kernels is less than the effect of FMC.

Measurement of transition temperatures. A DSC thermogram of temperature against corresponding MC, for aromatic rice at standard and low FMC, is plotted in Fig. 2. The three noticeable transitions (Tg, Tg2 & Tm) occur due to the starch properties of rice. The statistical averages of transition were a low transition temperature of about 45°C and 52°C, an intermediate transition temperature of 63°C and 71°C and a high transition temperature of 172°C and 173°C, for standard and low FMC, respectively. It should be stated that the first transition, Tg, is due to the collapse of the structure of the rice kernel, which changes from an immobilized to a flexible structure; this is considered to be the glass transition temperature. The intermediate transition (Tg2) is due to the evaporation of MC during the experiment. Biliaderis *et al*. (1993) and Perdon *et al*. (2000) observed several transitions in DSC thermograms for different varieties of rice, consistent with the results shown in Fig. 2.

There was a meaningful variation in the Tg with a reduction in MC. As expected, Tg increased as MC decreased. Statistical analysis indicated that the MC of starch has significant ($P \leq 0.05$) effects on its thermal properties (Table I). Changes in the MC during processing would affect the thermal properties of food, because water is

a very effective plasticizer and would reduce Tg (Slade & Levine, 1991). With an increase in drying temperature, the Tg decreased in both standard and low FMC treatments. At drying temperatures higher than Tg, rice kernels experienced a state transition from glassy to rubbery. In the glassy state, starch exists with low expansion coefficients, specific volume and diffusivity. By contrast, in the rubbery state, starch exists with higher expansion coefficients, specific volume and diffusivity. The changes in volumetric expansion and specific volume during glass transition have an effect on kernel fissuring and this is discussed in detail by Cnossen and Siebenmorgen (2000).

Pearson correlation between different properties of rice starches. The Pearson correlation coefficients for the relationship between the thermal and physical properties of aromatic rice kernels are shown in Table II. Transition temperature was negatively correlated to the MC of kernels ($r=-0.77$, $P\leq0.01$). A decrease in MC was accompanied by an increase in Tg. Transition temperature was not correlated with fissure parameters. This implies that the number of fissured grains doesn't change with an increase or decrease in the transition temperature, but, rather, that a change in the drying zone on the Tg line (i.e., from rubbery to glassy & vice versa) would create a fissure during the drying and post-drying periods.

Hypothetical paths on the glass transition line. Mapping the hypothetical path of the drying process on the DSC diagram relative to glass transition temperature may help us to better understand the mechanism of fissure creation during drying and post-drying periods. The drying process can be well explained using the concepts of Tg when FMC reaches standard and low levels, by superimposing the drying conditions on the rice state diagram (Fig. 3). From the previous results, most fissures occurred at a drying temperature higher than 40°C, during the drying and post-drying periods. As shown in Fig. 3, fissures occurred when an extended drying period caused grains to transform from a glassy state into a rubbery state, and proceeded further thereafter. Perdon *et al*. (2000) showed that the physical properties of a rice kernel changed dramatically as the kernel temperature passed through Tg. Prolonged high-temperature drying or low FMC render kernels more prone to fissure initiation due to a change in their state and consequently lead to HRY reductions. Samples dried at low temperatures (30°C & 40°C) remained in a glassy state; thus, little fissuring would be expected (Fig. 3).

With progressive drying at temperatures of 50 and 60°C, kernels experienced two state transitions in a relatively short period of time: first, from the glassy to the rubbery state due to the rapid temperature rise at the beginning of drying and then from the rubbery to the glassy state due to a rapid moisture loss. This double transition might increase the number of fissured kernels. This situation also occurred during the post-drying period. In samples dried at high temperatures, which far exceeded the maximum MC gradient, the percentage of fissured kernels did not decrease, even after a 12 h post-drying period at room temperature. The findings suggest that for drying temperatures higher than 50°C, drying process took place in the rubbery state, and that cool down at room temperature (below Tg) after drying might incur a dramatic increase in the number of fissured kernels.

The same procedure could also occur with bulk samples and individual kernels during the drying process. When bulk samples (batch dryer) are dried with air conditions near the Tg line, some kernels may be in the rubbery state while others may be in the glassy state. The difference in the MC of individual kernels might produce a different region within the kernel during the drying process. During the drying of samples at 50°C and 60°C, the surface of the rice kernels dried faster and transitioned from a rubbery to a glassy state, while the MC of the center portion remained high and still in the rubbery state. As drying progressed, the glassy area expanded gradually from the outer layers to the inner layers and occupied a larger volume. Because of these partial expansion and contraction effects, stress concentration may occur in the interface between the regions making grains prone to fissure initiation during drying and post-drying. This mechanism of fissure formation is supported by Yang and Jia (2004) who reported that the band between glassy and rubbery regions will gradually migrate inwards, layer by layer from the kernel surface, during the drying process. This condition would result in a high probability of fissure initiation. Perdon (1999) and Cnossen *et al*. (1999) reported that a state transition inside the kernels, from rubbery to glassy, could lead to rapid fissuring, which confirms the presented results.

CONCLUSION

Grains with a standard FMC subjected to low drying potential (30°C & 40°C) showed no significant increase in the number of fissured kernels due to increased post-drying duration. Regardless of drying temperature, the most fissured grain was produced within the first 12 h after drying. Therefore, at a given post-drying low FMC treatments significantly had higher fissured kernels than that other.

Tg was performed at a temperature about 45°C and 52°C for samples with standard and low FMC, respectively. Therefore, drying below than these Tg will help to decrease the formation of fissures. It can be concluded that a high drying temperature might have a more negative effect than a low FMC on the structure of kernels and affecting the thermal properties of the Kaori aromatic rice and leads to deterioration in its quality.

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