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Thermomechanical Property of Rice Kernels Studied by DMA

Hai-yan Jia, Dong Li, Yubin Lan, Bhesh Bhandari, John Shi, Xiao Dong Chen, and Zhi-huai Mao

Abstract

The thermomechanical property of the rice kernels was investigated using a dynamic mechanical analyzer (DMA). The length change of rice kernels with a loaded constant force along the major axis direction was detected during temperature scanning. The thermomechanical transition occurred in rice kernels when heated. The transition temperatures were determined as 47°C, 50°C and 56°C for the medium-grain rice with the moisture contents of 18.1%, 16.0% and 12.5% (wet basis), respectively. Length change of the rice kernels increased with the increase of the temperature and moisture content. Among the four rice varieties investigated, the results showed that the thermomechanical property was not significantly affected by variety.

KEYWORDS: rice, dynamic mechanical analysis, thermomechanical transition

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1. INTRODUCTION

Within the worldwide-cultivated cereals, rice is the most widely grown food grain crop among the oldest of cultivated crops and ranks, serving as the staple food for about half the world's population (Corrêa et al., 2007). World rice production in 2006 was approximately 630 million tons, while China growing more than one quarter of the total crop (International Rice Research Institute, 2006).

The moisture content of rice at harvest can be as high as 22-26% wet basis (w.b.), especially during the rainy season. In order to prevent deterioration after harvest, rice should be dried to a level of moisture content that can reduce respiration, inhibit mould growth, and prevent production of mycotoxins for safe storage (Dillahunty et al., 2000; Hu et al., 2003; Magan and Aldred, 2007). About 13-14% (w.b.) grain moisture is considered adequate for safe storage, milling and further storage as milled rice (Wiset et al., 2001).

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). The market price of broken grains is much less than intact rice as the poor cooking quality of broken rice (Li et al., 1999). The percentage of whole grain is the most important parameter for the rice processing industry. Head rice is comprised by milled kernels having lengths that are at least three-fourths of a whole kernel (Siebenmorgen and Cooper, 2006). Head rice yield (HRY) is the mass percentage of rough or unprocessed rice that remains as head rice after milling. HRY is the current standard to assess commercial rice milling quality. Therefore, reductions in HRY mean severe economic repercussions. Reductions in HRY cannot be universally attributed to one single factor; it can be influenced by environmental conditions during kernel development, maturation, harvest and especially postharvest treatments. Among all, post-harvest drying is the most critical parameter which influences the rice fissures and eventual increase in broken rice during milling. So, an effective drying process is required to produce optimal head rice yield. Rice kernel properties have been studied deeply for obtaining an optimal kernel treatment conditions during drying process and subsequent handling to minimize fissured kernels. A better understanding of the rice fissuring mechanism is significant for optimizing processing conditions and equipment design for improved milling quality of rice.

So far, many researches have done investigations on physical, chemical, thermal, and some mechanical properties of rice, mainly including the tensile strength (Kunze and Choudury, 1972; Kamst et al., 1999), compressive strength (Prasad and Gupta, 1973) and bending strength (Nguyen and Kunze, 1984; Lu and Siebenmorgen, 1995). Several characterization techniques, such as, differential scanning calorimetry (DSC) (Perdon, Siebenmorgen and Mauromoustakos, 2000; Cao, Nishiyama and Koide, 2004), thermomechanical analysis (TMA) (Perdon, Siebenmorgen and Mauromoustakos, 2000; Sun et al., 2002a), dynamic mechanical analysis (DMA) (Siebenmorgen, Yang and Sun, 2004; Chen et al., 2007) and Thermal Mechanical Compression Analysis (TMCT) (Truong et al., 2008) were used to investigate the properties of rice kernels. Through these characterization methods, some properties of rice kernels can be obtained, such as, thermal expansion coefficient, thermal conductivity, specific heat, and glass transition temperature. Recent researches using these characterization techniques showed that thermomechanical properties of rice kernels such as the glass transition temperature are important to rice drying and fissuring behavior (Perdon, Siebenmorgen and Mauromoustakos, 2000; Siebenmorgen, Yang and Sun, 2004; Cnossen and Siebenmorgen, 2000).

Rough rice is composed of husk, bran and white rice. It's a composite material consisting of several different biopolymers, including starch (mixture of amylose and amylopectin), which is the major constituent of milled rice at about 90% of the dry matter, proteins at about 8%, fat and other materials as a plasticizer (Zhou et al., 2002; Li et al., 2007; Sun et al., 2002b). Rough rice presents a very complex structure, partially crystalline, partially amorphous, comprising a number of components that can undergo glass transition process. It is therefore possible for thermomechanical transition, which is closely related to the structure and morphology of rice kernels, to occur during processes involving heating.

Dynamic mechanical analyzer (DMA) is a thermal analytical instrument used to test the mechanical properties of many different materials. It could be operated over a wide range of temperature and to determine changes in sample properties resulted from changes in five experimental variables: temperature, time, frequency, force, and strain. Dynamic mechanical analysis made over a wide range of time, temperature and frequency can provide much information on dynamic mechanical properties of material as a function of temperature, time, frequency, stress, and strain (Chen et al., 2007). The transition, molecular motions and ultimate properties of target material can be inferred precisely because the DMA has the features that are suitable for investigating the thermomechanical properties of rice kernel.

The objective of this study was to investigate the dynamic thermomechanical behavior of rice kernels as a function of temperature and moisture content. In this experiment, the length changes of the rice kernel under constant load were detected, while the temperature was rising. It should be point out that several different types of clamps including dual/single cantilever, three-point bending, tension, and compression are available for multiple test modes. Due to the clamps required the samples to be of a certain shape, only the compression clamp was suitable for rice kernels. As a result, the best choice was using the compression clamp for parallel compression experiment. The similar set-up was used previously by other researchers (Cao, Nishiyama and Koide, 2004; Siebenmorgen, Yang and Sun, 2004; Chen et al., 2007). The moisture loss of rice kernels should be avoided during the test. Without any protective measure, rice sample will get dried. Pereira and Oliverira (2000) tested the native wheat flour by simply wrapping the samples in aluminium foil to avoid moisture loss.

2. MATERIALS AND METHODS

2.1 Rice

IR-2 (long-grain), R894, NongLinLuNuo (medium-grain) and LiaoJing (four varieties, short-grain) having a typical harvest moisture content of 15% to 18% (w.b.), were obtained from ShangZhuang Experiment Station of China Agricultural University (CAU) in October 2007. After being threshed by hand and cleaned, all the rice varieties were immediately transported to the Drying Lab of College of Engineering, CAU. The rough rice samples from each variety were then dried at room temperature (23°C) for different times to different moisture content levels. The dried samples were sealed in polyethylene bags and stored in a refrigerator at 4°C. Before each experiment, the sample, enclosed in a bag, was equilibrated to room temperature (23°C). The moisture content of rough rice was determined by the oven drying method at 130°C for 24h (Jindal and Siebenmorgen, 1987).

2.2 Preparation of sample

Before the DMA testing, first, a rice kernel was randomly picked from each rough rice sample and then the selected sample for experiments was dehulled by hand with a tweezers to minimize any mechanical damages to rice kernel. The individual dimensions of each selected sample, length (*L*), width (*W*) and thickness (*T*) of grain were precisely measured using a digital vernier caliper (Fowler ProMax Electronic Caliper, 0-6", 0-150mm, Fred V. Fowler Co., Inc., Newton, MA 02466, United States) with accuracy of 0.01mm and used for calculating equivalent diameter for the experiment. The equivalent diameter (D_p) in mm considering a prolate spheroid shape for a rough rice grain, was calculated using following equation (Varnamkhasti et al., 2007):

$$D_{p} = \left(L\frac{(W+T)^{2}}{4}\right)^{\frac{1}{3}}$$
(1)

To obtain the approximate cylindrical shape with parallel end surface requirement for the compression test, both ends of the brown rice grain were cut with a thin blade, and then the two ends were abraded to smooth surface with emery paper (No.240, Beijing Dongsheng Coated Abrasive Industrial Co., Beijing, China). The length of prepared brown rice samples was approximately 2.5 mm for short-grain, 3.5mm for medium-grain and 4.5 mm for long-grain variety. In order to prevent moisture evaporation, each of the rough rice samples was individually wrapped completely on the top, bottom and side, with a thin layer of aluminum foil (Pereira and Oliveira, 2000). The prepared rice sample was placed in a standing position between two parallel compression cylindrical plates, with the major axis perpendicular to the lower cylindrical plate on the fixed clamp (*Figure 1*).



Figure 1. Schematic of the parallel compression clamp used and the standing position of prepared sample in the experiment.

2.3 Experiment method

A dynamic mechanical analyzer (DMA Q800, TA Instruments, New Castle, NJ, USA) was used to monitor the change in length of brown rice kernels applied constant force load (0.15N) along the major axis direction over the temperature range from room temperature (23°C) to 100°C. The samples were initially equilibrated at room temperature (23°C), held isothermally at 23°C for 5 min for thermal and mechanical equilibrium, and then heated using a linear temperature increase from 23°C to 100°C at a rate of 2.5°C /min, in the compression mode, with cylindrical plate geometry (plate diameter: 15 mm). After the DMA tests, the moisture content of the used samples were also checked by the oven method to ensure no significant moisture loss occurred during the experiments. At least five kernels from each variety at different moisture contents were used for DMA measurements.

3. RESULTS AND DISCUSSION

3.1 Curve description and analysis

When a material is subjected to a force, it deforms. During the uniaxial compression experiment, the rice kernel will resist the compression load force.

The compression stress (σ) of rice kernel relates to rice kernel strain (ε) by the well-known Hookean Law for an elastic body:

$$\sigma = E\varepsilon \tag{2}$$

where, E is Young's modulus of elasticity, a mechanical property of material. The compression stress (σ) of the rice kernel subjected could be calculated by:

$$\sigma = \frac{4P}{\pi D_p^2} \tag{3}$$

where, P is the compression force, D_p is the equivalent diameter of rice kernel. The relation between the strain (ϵ) and the length (l) of prepared rice sample is expressed as following:

$$\varepsilon = \frac{\Delta l}{l} \tag{4}$$

where, *l* is the length of prepared rice sample, Δl is the change value of the length. According to the equations (2), (3) and (4), the expression of the length change could be deduced as following:

$$\Delta l = K \cdot \frac{1}{E} \tag{5}$$

and value of factor K is given as:

$$K = \frac{4Pl}{\pi D_p^2} \tag{6}$$

it should be explained that value of factor K didn't change for the individual rice, because the values of all the parameter in the expression (6) were not variable in the experiment, while they were given or measured.

Figure 2 shows typical plot of the length change of the rice kernel as a function of temperature, the axis of coordinate Y denotes the displacement of upper cylindrical plate equivalent to the length change of rice. As shown in Figure 2, almost no length change of rice kernel was observed at the beginning of the heating (between 23°C and around 30°C). Beyond 30°C, the initiation of length change was observed, suggesting that the softening of the rice kernel started at around 30°C. With the temperature rise, the length of the rice kernel decreased slowly, then the reduction of length was accelerated. At last the length change of the rice was nearly linear with the temperature. According to the equation (5), it

can be assumed that Young's modulus of elasticity (E) related to the length change of the rice kernel is variable, and it's inversed with the length change of the rice kernel. This means that the Young's modulus (E) of the rice kernel is also a function of temperature. The Young's modulus (E) of the rice kernel showed almost no change at the beginning of the experiment, with the increase of temperature, the modulus decreased slowly, and then the reduction of modulus was accelerated. This finding is similar with that of Chen et al (2007), who observed the storage modulus change against temperature in a DMA analysis for dynamic viscoelastic properties of rice kernels. Therefore, it can be inferred that some state phase change occurred in the rice kernel during the heat scanning.



Figure 2. The length change of rice kernel against temperature curve for the brown rice kernel (IR-2, long-grain) with a moisture content of 15.9% wet basis (w.b.). Both solid lines are the tangential lines of the curve.

3.2 Thermomechanical transition

As previously mentioned, about 90% of the milled rice dry matter is starch. Rice starch is a semicrystalline polymer that comprises highly branched, partially crystalline amylopectin molecules and amorphous amylose molecules. The molecular motion of the polymer chains in an amorphous polymer at a lower temperature is immobilized in a random conformation, rendering it glassy and brittle. If sufficient heat is supplied to the polymer, molecular motion is restored and molecules can slide against one another as the polymer becomes viscous, rubbery, and flexible (Yang and Jia, 2004). Such a physical change from an immobilized conformation to a flexible structure, which reflects an increase in motion of major segments of the polymer backbone, is called the glass transition, one of the thermomechanical transitions. The glass transition is associated with the onset of long range cooperative segmental mobility in the amorphous phase, in either an amorphous or semicrystalline polymer.

In this test, the length change of rice sample detected by the DMA as a function of temperature indirectly showed that the Young's modulus of rice was variable. And there was a thermomechanical transition (or glass transition) during heating. This transition has especially been attributed to molecular mobility within the starch fraction since the major component of rice is starch.

To determine the temperature at which the thermomechanical transition was occurred, two tangential lines were drawn on *Figure 2*: one at the start of the descending stage, and the other at the end of the descending stage of the curve. The temperature corresponding to the junction of these two tangential lines is as glass transition temperature (T_g). So, the T_g value of IR-2 with a moisture content of 15.9% (w.b.) was 55±2°C, which is higher than the T_g value (48±5°C) of rice kernel with the same moisture content reported by Siebenmorgen et al. (2004).

3.3 Effects of variety and moisture content

The length change of the long-, medium- and short-grain varieties at the similar moisture contents versus temperature is shown in *Figure 3*. As can be seen from the curves, the length change inflections of the long-, medium- and short-grain rice kernels against temperature compared closely. The statistical tests indicated that the data sets were not significantly different from each other (P= 0.367). So, the thermomechanical transitions of different varieties were similar. This finding is consistent with that of Perdon et al. (2000), who observed no statistical differences in T_g by TMA between medium-grain and long-grain varieties.



Figure 3. The length change of rice kernel against temperature curves for three varieties of brown rice kernels (IR-2, long-grain; NongLinLuNuo, medium-grain; LiaoJing, short-grain) with the moisture contents of 16.0±0.5%.

The length changes against temperature curves of one single rice variety (R894, medium-grain) at different moisture contents are illustrated in Figure 4. As can be see from the curves, the length change of the rice at higher moisture content is larger than that at the lower moisture content at a given temperature. Statistical tests indicated that the data sets of the length change of rice at different moisture content levels were obviously different from each other (P<0.0001). The transition temperatures were determined by two tangential lines method as 47°C, 50°C and 56°C for the medium grain with the moisture contents of 18.1%, 16.0% and 12.5% (w.b.), respectively. It is clear that the thermomechanical transition temperatures of the rice kernels are inversely dependent on moisture content, which is consistent with previous results (Perdon et al., 2000; Sun et al., 2002b). The temperature of the transition increased as moisture content decreased, confirming that moisture acted as a plasticizer in the rice kernels. Plasticizers are small molecules that soften the polymer by lowering its glass transition temperature or reducing its crystallinity or melting temperature (Sperling, 2005). Since the size of the water molecule is smaller than the starch macromolecules, the water molecules can be more inclined to move. When the temperature is increased, the motion of the water molecules could produce more free volume at molecular level, as a result, there will be an enough space for the motion of chain

segments of polymer molecules. Thus, the moisture contents will influence the thermomechanical transition of the rice kernels.



Figure 4. The length change of the one single rice variety (R894, medium-grain) versus temperature curves with various moisture contents.

4. CONCLUSIONS

The results show that the Young's modulus of rice kernels is a function of temperature. The modulus change is attributed to the increase of molecular mobility in the starch fraction with the increase of temperature, consequently resulting in the thermomechanical transition. The thermomechanical property was not significantly affected by variety. The thermomechanical transition temperatures of the rice kernels are inversely proportional to the moisture content. The transition temperatures were determined as 47°C, 50°C and 56°C for the R894 (medium-grain) variety with the moisture contents of 18.1%, 16.0% and 12.5% wet basis, respectively.

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