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A new method to determine viscoelastic properties of corn grits during cooking and drying

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Abstract

The working principles and the theoretical background of a new method to measure the viscoelastic properties of grains during cooking and drying processes are presented. Specifically, corn grits at different processing stages of cooking and drying were chosen as the model grain and their viscoelastic characteristics, namely elastic stiffness and viscous damping, were determined. During the measurements grits were squeezed between a rigid bottom plate and a top round element oscillating at random frequencies in a range 10–10,000 rad/s. A frequency response of the mechanical impedance of the samples, which is defined as the ratio between the force applied to the samples and the oscillation velocity, was obtained. Corn grits were measured in their raw state, after cooking in a pressure cooker for different times (2, 7, 15, 30, and 60 min), and at different times of drying (30, 60, and 120 min) at 65 °C. The measured mechanical impedances of the samples showed that rheological changes upon processing can be monitored by the newly developed method. Non-destructive and quick measurements, data covering a wide range of frequencies, and the adaptability of the method to be used with available instruments used in texture measurement such as texture analyzers are some of the important advantages that the new method provides to the area of cereal processing.

Keywords: Cereal; Corn; Texture analysis; Viscoelastic

1. Introduction

The manufacture of cereal flakes begins with two major processing steps which include the cooking and drying of the flaking grains. These process steps prepare the grain for the flaking process. Many important physical and rheological changes occur during the cooking and drying of grains mainly due to changes in their moisture content and physicochemical changes mostly associated with starch gelatinization and retrogradation. The cooking process promotes a softening of the grits due to the intake of water and gelatinization of the starch, whereas drying promotes the hardening of the grains due to water desorption and possible retrogradation of the starch. These changes are important because they can affect subsequent operations, specifically flaking and toasting, which may ultimately affect final textural, and sensory attributes of the final product.

The process of cooking involves the heating of the cereal at high temperatures and high moisture in pressurized cookers, which results in the diffusion of water into the endosperm of the corn grits, thus making them softer and easier to process. Additionally, the presence of water in the grits, and the addition of heat during the cooking process favor the gelatinization of the starch. During starch gelatinization, the structure of the starch granules changes from a semi-crystalline to an amorphous state which is often characterized by the dissociation of double helices (crystalline regions) and the swelling of granules (Tester and Debon, 2000). Gelatinization is also inherently responsible for enhancing the cereal's digestibility, textural/sensory properties, and palatability of the final product. The conventional method for cooking flaking grits intended for the manufacture of cornflakes involves the use of steam batch cooking of corn grits to a final moisture

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of 30–35% (wet basis) and pressure 15–21 psi (Shukla, 1999). This method occurs in the absence of shear and with restricted water (Caldwell et al., 1990).

The process of drying requires the contact of a heated air-flow with the cooked grits, thereby decreasing their moisture content to values that are suitable for flaking. Typically, cooked grits for corn flake processing are dried from an initial moisture content of 33–35% (w.b.) on vats for 1–5 h until a moisture of 15–21% (w.b.) is achieved (Shukla, 1999). Drying creates an uneven moisture distribution in the grits. Surface drying caused by the heated airflow leaves the grits with a low outer moisture content and a high inner moisture content. During this step, if the grits are dried too rapidly, the grits will case harden and form a hard outer shell that resists moisture diffusion. The non-uniform moisture distribution present in the grits at the end of the drying phase is corrected by an additional tempering step. It is believed that the primary purpose of the tempering step is to equilibrate this unequal moisture distribution. However, it has been speculated that during tempering the gelatinized starch molecules undergo some physicochemical transformations (Caldwell et al., 1990). During drying, the moisture content of cereal grains is decreased and hardness generally increases. Hardness is a relative term used in the cereal industry that is mostly dependent on both the final cooking and drying moisture contents of the cereal. Hardness of cereal grains prior to flaking can affect power requirements during this process as well as the damage undergone by their starch components. Damage of starch during processing is extremely important because it has been shown that it can lead to the decrease in the bowl-life of cereal products (Wright, 2005).

The processes of cooking and drying are commonly utilized in the cereal processing industry; however, the issue of completeness and its effect on subsequent operations in either case is more of an art than a science. The ability to know quickly how well a sample is cooked and/or dried and how moisture affects its rheological properties is currently lacking in the industry.

The objective of this study was to develop and test a rapid and novel method to monitor and measure the mechanical properties of a single cereal grain during the processes of cooking and drying. Ultimately, this method may find suitable applications in industrial online/at-line systems due to its non-invasiveness, little to no modification of the testing samples, and its ability to obtain quick and instantaneous measurements on the rheological properties of the samples using existing commercial testing equipment like texture analyzers. These are obvious advantages when monitoring of dynamic processes is desired.

1.1. Theoretical background and measurement

Oscillatory testing is commonly used in classical rheology for the determination of mechanical properties of viscoelastic materials. The method proposed in this study also applies oscillatory testing, but in compression rather than shear as typically used in conventional rheology. In the method proposed in this study the sample resonates when it is excited using random frequencies between 10 and 10,000 rad/s. From the resulting frequency response the corresponding viscoelastic properties can be obtained. Resonant frequency methods have been extensively used in rheology and general details of these techniques are given in specialized rheology books (Ferry 1980, Bird et al., 1987). In previously used resonant frequency-based methods a probe, which is in contact to fluid samples, is oscillated inside the sample. Then, the sample viscoelastic properties are obtained by the analysis of the probe oscillation. The instrument's stiffness, internal damping and mass are usually the limiting factors in these measurements because instrument's stiffness or damping can interfere with those of the sample leading to measurements with reduced sensitivity. Moreover, they cannot be applied to irregularly shaped solid samples like for example corn grits. Figs. 1 and 2 show a schematic of the proposed method for testing corn grit samples. Corn grit samples are placed between one roundly shaped element and a stationary bottom plate. The top element has a diameter that is smaller than the corn grits, and thus it can be assumed that while the element touches the sample it applies a load on the sample center. This testing geometry is necessary due the irregular shape of corn grits. When the top round element applies a harmonic force on the grit sample the oscillation phenomena can be described as a lumped oscillating system composed of a mass, stiffness s, and damping R. The equation of motion for the force excited spring-mass-damper system, schematically de-

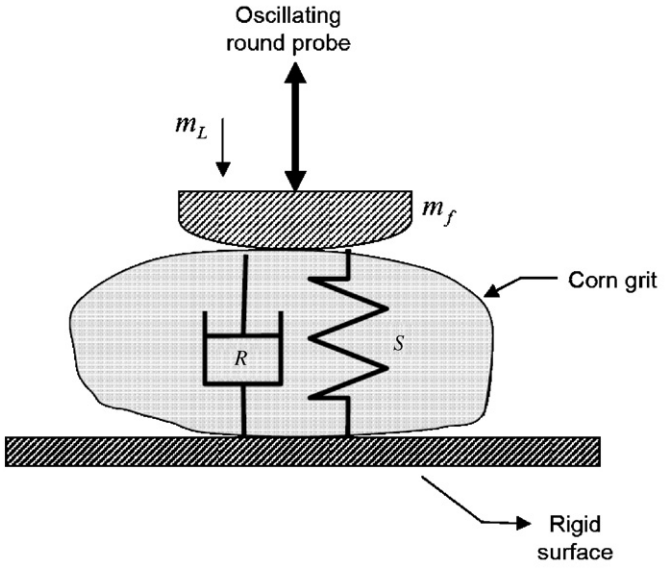

Fig. 1. Schematic of the mechanical model used to describe the mechanical properties of the corn grit samples. Stiffness, s, provides the elastic characteristics of the sample whereas damping, R, provides the viscous characteristics of the corn grit samples.

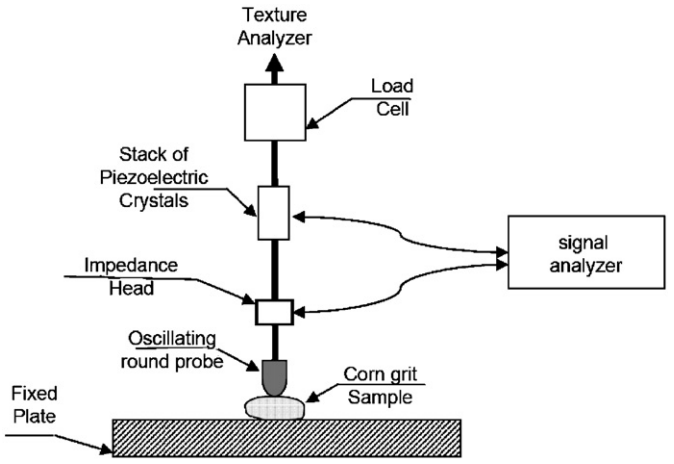

Fig. 2. Schematic of the testing apparatus.

scribed in Fig. 1, can be expressed as (Ferry, 1980):

$$F(t) = m\dot{u}(t) + Ru(t) + s\int u(t)\,\mathrm{d}t, \tag{1}$$

where $F(t)$ is the momentary force, t is time, and s and R are the stiffness and damping of the sample. The symbols $\dot{u}$, u, $\int u(t)$ denote acceleration, velocity and displacement of the mass (m), respectively. The mass of the system is simply the sum of mass of the top element (m_e), and the initial load (m_L) applied to the sample during the measurement. For a harmonic excitation it is more convenient to express Eq. (1) in complex form which can be achieved by applying the Fourier transformation to Eq. (1) to give

$$\hat{F}\cdot e^{i\omega t} = i\omega m\hat{u}\cdot e^{i\omega t} + R\hat{u}\cdot e^{i\omega t} - \frac{i\,s}{\omega}\hat{u}\cdot e^{i\omega t}, \tag{2}$$

where $\hat{F}$ and $\hat{u}$ are time-independent complex quantities related to the force and the velocity, respectively which contain amplitude and phase information of the harmonic motion, ω is the angular frequency and i is $\sqrt{-1}$. A convenient parameter is defined as the ratio between the Fourier transformed force and velocity and is called mechanical impedance $\hat{Z}$ (Harris and Piersol, 2001). It can be obtained from Eq. (2) as

$$\hat{Z} = \frac{\hat{F}}{\hat{u}} = R + i\left(\omega m - \frac{s}{\omega}\right). \tag{3}$$

Mechanical impedance $\hat{Z}$, is the property measured in the proposed method. As it is defined in terms of the Fourier transformed force and velocity, that is in the frequency domain, it is a quantity related to the frequency response of the test and represented by a complex number. As expressed in Eq. (3) the real part of the complex mechanical impedance R is related to the damping characteristics of the sample whereas the imaginary part contains information related to the stiffness of the sample in addition to the inertia of the measuring system given by the factor ωm. One of the important advantages of the proposed method over other resonant frequency methods is that this system does not have any internal stiffness and damping. Hence measured R and s values of the sample are not affected by the damping and stiffness of the instrument. The small mass of the instrument, m_e, is another important advantage because it keeps the inertia low so that sample stiffness s can be measured at significantly high frequencies without affecting sensitivity. This is not the case in conventional oscillatory measurement systems. As discussed and indicated by Eq. (3) damping can be easily obtained from the real part of the frequency response of the system. However, obtaining the stiffness s requires one additional step because two different masses have to be considered in the term $i\omega m$. As discussed the total mass is $m = m_e + m_L$. Both m_e and m_L are known from the weight of the measurement system and the load applied to the sample, respectively, therefore sample stiffness can be obtained from the imaginary part of $\hat{Z}$ (see Eq. (3)) as

$$s = \omega^2 m - \omega\,\mathrm{Im}(\hat{Z}), \tag{4}$$

where $\mathrm{Im}(\hat{Z})$ is the imaginary part of the measured complex impedance $\hat{Z}$.

For cylindrically shaped samples squeezed between two parallel plates the values, R and s, could be used to obtain viscoelastic quantities such as the complex viscosity η^*. The complex viscosity η^* is defined in terms of two viscoelastic properties known as the out of phase η' and in-phase η'' viscosities, respectively by the equation $\eta' - i\eta''$ (Ferry, 1980). These viscoelastic properties can be related to the real (Re) and imaginary (Im) parts of Eq. (3) following the work of Field et al. (1996):

$$\mathrm{Re}(\hat{Z}) = \frac{3\pi a^4\eta'}{2h_o^3}, \qquad \mathrm{Im}(\hat{Z}) = \frac{3\pi a^4\eta''}{2h_o^3} - \frac{3m\omega a^2}{20h_o^2}, \tag{5}$$

where a is radius and h_o is height of the cylindrical shaped samples. Since the complex modulus G^* can be expressed as (Ferry, 1980)

$$G^* = G' + iG'' = i\omega\eta^* \tag{6}$$

the loss modulus (G'') and the elastic modulus (G') could be easily obtained from Eqs. (5) and (6). Testing cylindrical samples, however, involves significant sample preparation (e.g. cutting), which defy the main purpose of this study concerning the development of a non-destructive and ready to use technique to determine viscoelastic properties of processed cereal grains. In that sense, the values of R and s are preferred to characterize the viscous and elastic components of corn grits. Since the diameter of the round probe was smaller than that of the grit, only the localized area of the grit which is in contact with the probe, is deformed. Furthermore, due to the small deformation and the relatively high stiffness of the sample it can be assumed that the contact area does not change during the oscillation. Thus, the obtained damping and stiffness properties of the samples can be attributed to the material localized below the probe.

2. Materials and methods

2.1. Cooking and drying of corn grits

Grits of 5–6 mm diameter were prepared for measurements in their raw state and during the cooking and drying processes. The cooking process consisted of heating corn grits with the addition of water (1:1 by weight) under a pressure of 18 psi in a Farberware 4 Qt. pressure cooker (FPC 400, Salton Inc., Illinois, USA) for different times (2, 7, 15, 30, and 60 min). Final moisture content at the end of 60 min cooking was approximately 51% (w.b.). Dried grits were obtained from the 60 min cooked grits by drying them at different times (30, 60, and 120 min) at 65 °C. Grits dried for 120 min had an approximate moisture content of 18% (w.b.). All grit samples, whether raw, cooked, or dried, were measured at room temperature (23 °C).

2.2. Instrument setup

For testing, the grits were placed between an oscillating spherically round probe having a diameter of 1 mm and a rigid surface (Fig. 2). The design used a stack of piezoelectric crystals attached to an impedance head (B&K Model 8001, Denmark). Upon the application of voltage using a DSP Siglab (Dynamic Signal Analysis System, Spectral Dynamics, San Jose, California, USA), the upper fixture oscillated, and force and acceleration were obtained through the impedance head and transformed into a frequency response by the DSP Siglab software. During measurements, the magnitude of the force and displacement changed with frequency. Especially at resonance, the displacement reached a maximum. Typical forces applied to the sample were between 0.1 and 0.4 N. Displacements were less than 10 μm. All the moving components of the measurement system, shown in Fig. 2, were attached to a Texture Analyzer (Texture Technologies, MA, USA) and the built-in force and height controls of this instrument were used to set the test. Specifically, the Texture Analyzer load cell was used to monitor the normal force applied on the grit samples so that they could be oscillated under constant normal loads. During measurements m_L was adjusted to 0.5 N for all the samples. Since it was desired to use the same load for all the samples, optimization of the normal load was required. In general, high loads could be applied to raw and dried samples, but that force may not be applicable for cooked samples because of their more fragile structure. Thus, prior to the measurements a suitable normal load of 0.5 N was found suitable for both hard (raw) and soft (60 min cooked) samples, i.e. the hardest and softest samples.

3. Results and discussion

By analyzing the results of the test using the proposed method it is necessary to consider that a harmonic force is applied to the corn grit sample and the resulting velocity response is measured. Since the natural resonance frequency of any system is defined as the frequency at which the test response is a maximum (in this case the measured velocity), the impedance values become minimum as a result of natural resonance of the sample. In harmonic analysis it is a common practice to represent and identify resonance frequency as a peak, therefore the reciprocal of the measured impedance, called mobility, is generally used as the frequency response curve of the test. Typical mobility values of the corn grits obtained at different moisture contents are given in Fig. 3. These moisture contents were achieved by cooking the grits at different times. As shown in the figure, corn grits resonated at lower frequencies as the moisture content increased. Since the resonance frequency ($f_{resonace}$) of the sample can be obtained from the maximum of the absolute value of the mobility (i.e., $|1/\hat{Z}|$) then from Eq. (3) the resonance frequency $f_{resonace}$ is estimated as $\sqrt{s/m}$. Thus, decreases in resonance frequencies are an indication of softer corn grits, i.e. having lower stiffness. An exponential relation between the percent moisture content (M) and the grit stiffness s was obtained from the data as $s = 3.75*10^5*e^{0.17M}$ with $R^2 = 0.999$. Another observed characteristic among the frequency response curves of the different corn grit samples was the amplitude of the resonance peaks. As shown in Fig. 3 amplitude of the mobility peaks increases as the moisture content rises. This trend was caused by the decreasing of the damping (R) at the higher moisture content of grits. This behavior is similar than the decreases in the storage modulus G' of a viscoelastic material with increases in moisture contents. The behavior can be explained mathematically through Eq. (3). The mobility of the corn grit samples is the reciprocal of the impedance given by Eq. (3). At the resonance frequency the imaginary part of the measured impedance $\hat{Z}$ Eq. (3) is equal to zero, consequently the mobility becomes equal to $1/R$. In other words, at the resonance frequency the observed increase in

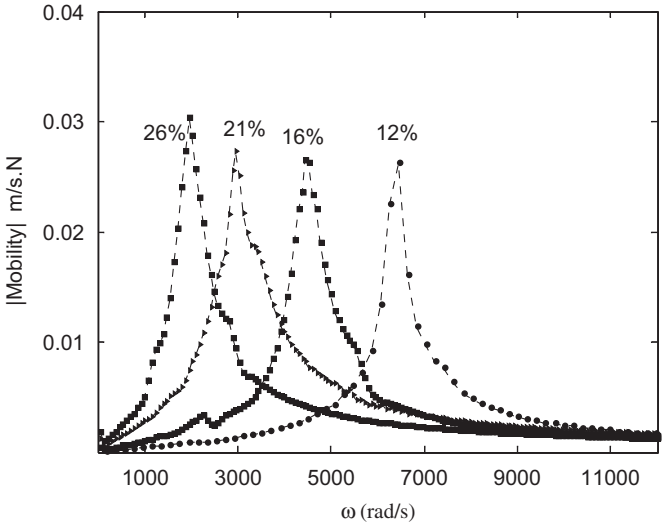

Fig. 3. Mobilities of corn grit samples at various moisture content levels.

mobility of the grits samples when moisture increases could be attributed to a reduction in the damping of the sample R.

The effect of cooking time on the viscoelastic properties of individual corn flaking grits was also investigated using the proposed technique. Fig. 4 shows the effect of cooking time on the mobility of the samples. As cooking time increased a gradual softening of the sample occurred primarily due to water absorption into the endosperm of the grain. As indicated in the figure the resonance frequency for longer cooking periods was always lower than that of the shorter cooking periods. The position of the resonance frequency is not the only way to determine the degree of stiffness of the corn grit samples. Fig. 5 depicts stiffness values, s, of the samples calculated by Eq. (4). As shown, raw corn grits were significantly stiffer compared to the cooked samples, and longer cooking times further decrease the sample stiffness.

Fig. 6 illustrates the effect of cooking time on the measured damping R. It is shown that cooking time decreased the value of R as a consequence of the increase in moisture content of the samples during cooking. Fig. 6 also shows a pronounced decrease of the damping R values with increasing frequency. These curves show similar trends as those observed in η'' or G'' versus ω curves of other viscoelastic materials tested in commercial rheometers. The effect of drying time on the mobility of corn grits is illustrated in Fig. 7. As explained raw samples were cooked for 60 min, then the samples were dried for 30, 60, and 120 min. As shown in the figure cooking for 60 min significantly decreased the stiffness (resonance frequency) of the samples. Then, the stiffness of the samples increased as a result of drying and the reduction of the samples

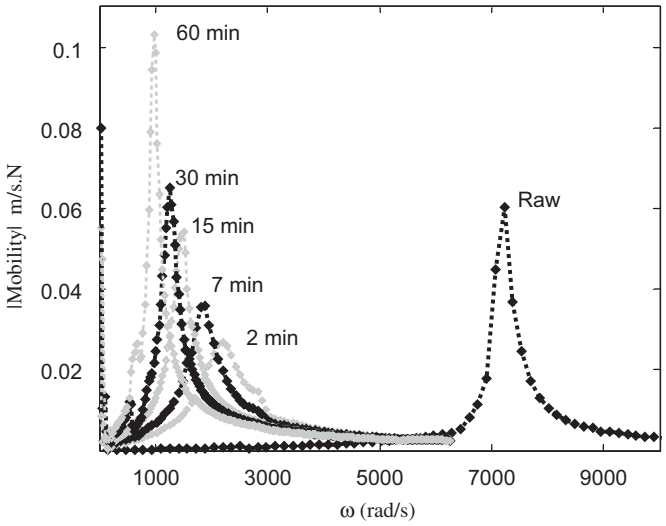

Fig. 4. Mobilities of corn grit samples cooked for different times.

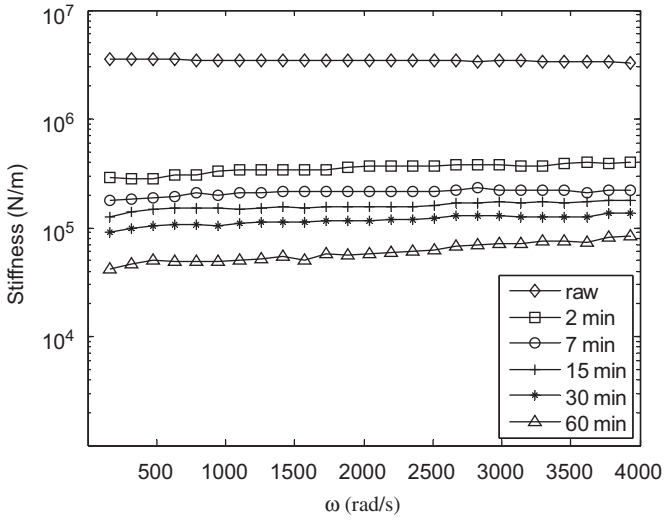

Fig. 5. Stiffness of corn grit samples cooked for different times.

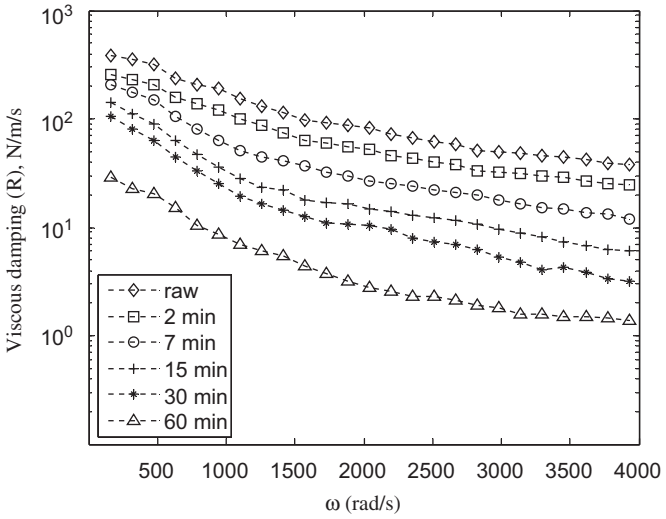

Fig. 6. Damping, R, of corn grit samples cooked for different times.

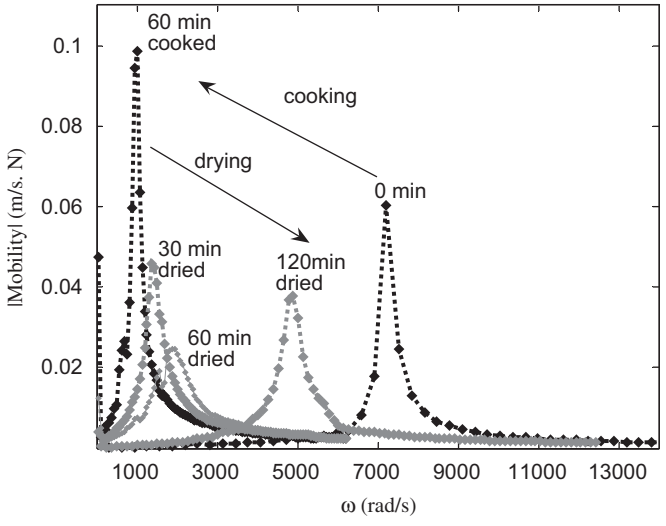

Fig. 7. Effect of cooking time and drying times on the measured mobilities of corn grit samples.

moisture contents. Longer drying time resulted in harder grits as expected. This behavior is also clearly shown in the calculated values of the stiffness s which are shown in Fig. 8. For the case of damping or viscous losses it was difficult to get enough information from Fig. 7 because the samples resonated in a wide range of frequencies. However, when R values were calculated and plotted as shown in Fig. 9, the 60 min cooked sample had the lowest viscous damping and the 120 min dried sample exhibited the greatest viscous damping. Although the 120 min dried samples had a moisture content approximately 6% higher and lower stiffness than those of the raw grits they exhibited higher viscous damping R probably as a result of structural changes such as retrogradation.

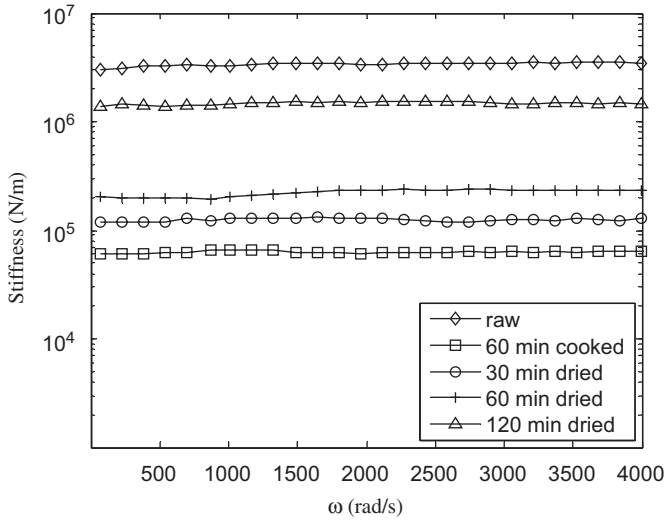

Fig. 8. Effect of cooking time and drying times on the stiffness of corn grit samples.

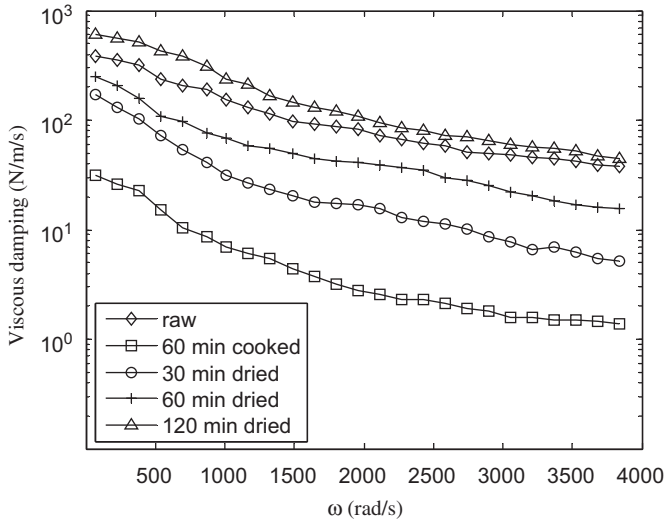

Fig. 9. Effect of cooking time and drying times on the viscous damping of corn grit samples.

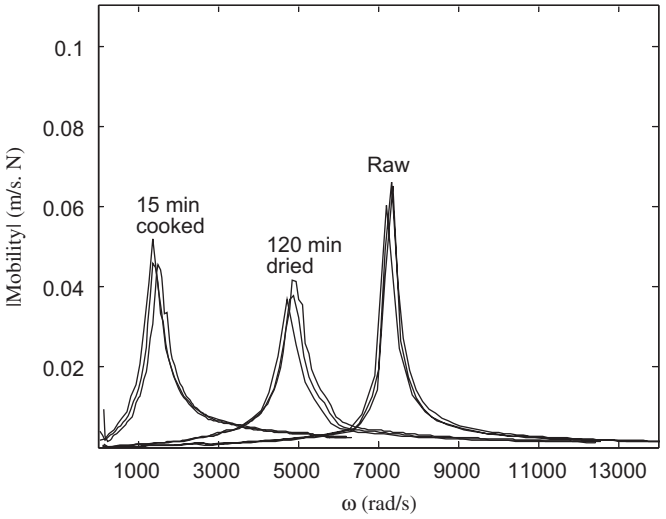

Fig. 10. Repeatability of measured mobilities.

3.1. Experimental errors and measurement repeatability

Fig. 10 shows typical repeatability of the mobility measurements. In general variations in the amplitudes of resonance peaks are smaller than those observed in the position or the resonance frequencies. That is attributed to the irregular shape of the sample. However, the use of the roundly shaped probe helped to reduce that inherent variability. During measurements a harmonic force was applied on the center of the sample instead of squeezing samples. Because the grit samples did not have well-defined geometries, the use of roundly spherical probes had some advantages. It was observed that this approach significantly reduced the effect of irregular shapes in the testing repeatability. There are also other errors inherent to the measurement system and signal processing such as converting time data to frequency data via Fast Fourier Transform; details of these errors and how to estimate them are given by Mert et al. (2003, 2004).

4. Conclusions

The rheological changes that occur in corn flaking grits during the processes of cooking and drying were successfully measured and monitored using a novel method described in this work. The softening effect that occurs during the cooking process was mainly attributed to the absorption of moisture and the gelatinization of the starch during the cooking process. Similarly, the hardening effect that occurs during drying is mainly attributed to the loss of moisture and surface hardening, and possibly retrogradation of the starch molecules. Achieving "fully cooked" grits at acceptable moisture contents of dried grits for milling have long been the result of trial-and-error and the knowledge of experienced operators. The ability to know quickly at what state a sample is along its processing history is currently lacking in the cereal and food industry.

The method proposed in this study may offer the possibility of a rapid and accurate determination of the sample rheology and how it is affected by the different processing conditions. Thus, the proposed method may find suitable applications in industrial online/at-line measurement systems on cereal processing due to its non-invasiveness and little to no modification of the testing samples. Moreover, the instrument can be easily used with commonly available universal testing machines instruments such as the Texture Analyzer.

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