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Viscoelastic behavior of maize kernel studied by dynamic mechanical analyzer

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ABSTRACT

The creep recovery, stress relaxation, temperature-dependence and their frequency-dependence of maize kernel were determined within a moisture content range of 11.9% to 25.9% (w/w) by using a dynamic mechanical analyzer. The 4-element Burgers model was found to adequately represent the creep behavior of the maize seeds ($R^2 > 0.97$). The 5-element Maxwell model was able to better predict the stress relaxation behavior of maize kernel than the 3-element Maxwell model. The T_g values for the maize kernels decreased with increased moisture content. For example, the T_g values were 114 °C and 65 °C at moisture content values of 11.9% (w/w) and 25.9% (w/w), respectively. The magnitude of the loss moduli and loss tangent and their rate of change with frequency were highest at 20.7% and lowest at 11.9% moisture contents. The maize kernel structure exhibited A-type crystalline pattern and the microstructure was found to expand with increase in moisture content.

1. Introduction

Maize is widely grown in many countries including China and it is an important staple food for human as well as animal. The moisture content of maize when it is harvested varies from 25% to 35% (Marques da Silva & Silva, 2006) which is not suitable for storage. When maize kernels having high moisture contents are stored, they undergo certain degree of shrinkage in their outer dimension due to loss of moisture. Food products exhibit quite different mechanical behavior because they are comprised of different macromolecules such as carbohydrates, proteins, cellulose (Gunasekaran & Mehmet, 2000). Most food products show viscous and elastic behaviors at the same time because they are neither pure liquids nor pure solids. When external force is applied to a viscoelastic food material it requires a certain time to get to its new dimension. Furthermore, when food materials are subjected to deforming external force, they cannot return to their original dimensions due to the fact they are not purely elastic (Del Nobile, Chillo, Mentana, & Baiano, 2007b).Many researchers have applied dynamic mechanical analyzer (DMA) to determine the mechanical and structural changes in a number of materials such as frozen wheat dough (Laaksonen & Roos, 2000), sweet potato (Li, Li, Wang, Özkan, & Mao, 2010), starch films (Zhou et al., 2009), rice kernels (Chen et al., 2007), flaxseed gum based edible films (Wang, Li, Wang, Yang, & Özkan, 2011), cooked rice (Chang et al., 2009), corn kernels (Hundal & Takhar, 2009), potato (Blahovec & Lahodová, 2009).

Spring and dashpot based mechanical models (combined in different ways) are used for describing the mechanical behavior of a viscoelastic material where the spring represents an ideal elastic behavior and the dashpot represents an ideal viscous behavior (Del Nobile et al., 2007b). Maxwell, Kelvin–Voigt and standard linear solid models are most commonly used mechanical models (Bruno & Moresi, 2004; Correia & Mittal, 2002) to represent the viscoelastic nature of food materials. The Maxwell model consists of a Hookean spring and a Newtonian dashpot in series (Mohsenin and Mittal, 1977) and this model is used to represent the stress relaxation data without considering the equilibrium stress. By using a generalized Maxwell model which consists of several spring elements in parallel, the viscoelastic behavior of food materials can be described better (Steffe, 1992). Stress relaxation data are very important because they provide greater insights of phenomena such as fruit ripening (Hassa, Alhamdan, & Elansari, 2005), fruit firmness (Blahovec, 1996), staling of cereal products (Limanond,

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E_1	elastic modulus (MPa)
E_2	elastic modulus (MPa)
E_c	equilibrium elastic modulus (MPa)
G'	storage modulus (MPa)
G''	loss modulus (MPa)
P	elastic modulus (MPa)
R^2	correlation coefficient (dimensionless)
T_g	glass transition temperature (°C)
$\tan\delta$	loss factor (dimensionless)
η	viscosity (MPa s)
τ_1	relaxation time (s)
τ_2	relaxation time (s)
τ_r	retardation time (s)
σ	stress (MPa)
ε	strain (dimensionless)

Castell-Perez, & Moreira, 2002) and checking phenomenon in crackers (Kim & Okos, 1999). The Kelvin–Voigt model is composed of a spring and a dashpot in parallel and it better represents the earlier stage of creep development. It has also been reported that the viscoelastic behavior of biological materials is better modeled by the Burgers model which is comprised of a Kelvin and a Maxwell element in series (Steffe, 1992). One of the Burgers models consisting of one Maxwell element in series with two Kelvin–Voight elements describes the liquid-like viscoelastic behavior reasonably well (Mitchell & Blanshard, 1976). Another Burgers model consisting one spring and two Maxwell elements was successfully used to describe the stress relaxation of lipids such as beeswax, candelilla wax, carnauba wax and a high-melting milk fat (Shellhammer, Rumsey, & Krochta, 1997). Models containing more exponential components and a residual terms have been used to describe the stress relaxation behavior of cheese (Masi, 1989).The kinetics of corn tortilla staling through stress relaxation data was modeled by Limanond et al. (2002) and (Hort, 1997). These authors found that a 7-element generalized Maxwell model fits the data better than the three and 5-element models. Mancini, Moresi, and Rancini (1999) were able to describe the viscoelastic behavior of several alginate gels by using a generalized Maxwell model consisting 5 elements. The stress relaxation data of potatoes obtained by using compression mode of texture analysis were modeled with a five parameter generalized Maxwell model (Finca & Dejmek, 2003).

The frequency scanning test which is usually carried to liquid samples by using DMA can provide better insights into the melting behavior of food materials (Li et al., 2010). It has been shown that the viscous or liquid-like behavior predominates in the low frequency range while elastic or solid-like behavior is dominant at relatively high frequencies. (Menard, 1999b).

The viscoelastic behavior of maize seeds was investigated in this study in terms of creep-recovery, stress relaxation, temperature dependence, and frequency dependence of the viscoelastic properties (elastic and loss moduli, loss tangent). We also modeled the creep-recovery and relaxation behaviors of the maize kernel using the data obtained from DMA.

2. Materials and methods

2.1. Materials

The Zhengdan 958 maize cultivar was harvested in Gansu province of China in September and its seed kernels were transported to Drying Laboratory of China Agricultural University (Beijing) for this study. These seeds were stored in double layered ziplock bags in a refrigerator at 4 °C before further tests. The initial moisture content of the maize seed samples was 25.9% (w/w) (at 20 °C, 9%RH).

2.2. Sample preparation

The maize seed were dried in an oven in one or two (thin) layers. Batches of seed samples were dried at different times (at 40 °C) in order to retain different moisture content (11.9%, 14.6%, 16.4%, 20.7%, 23%, 25.9%, w/w). After drying, each batch of the sample was sealed in double layered ziplock bags and the headspace air was removed by vacuuming. The moisture content of the seed samples was allowed to reach equilibrium by storing in a refrigerator at 4 °C. The moisture content of each dried sample was measured by Single Kernel Moisture Tester (GTR800E, Shizuoka Seiki, Japan).The samples were dried to six different moisture contents (11.9%, 14.6%, 16.4%, 20.7%, 23%, 25.9%, w/w). By using commercial sand paper, the samples were sanded to a flat uniform smooth surface. To avoid any mechanical damage to the samples, the samples sanded manually exercising utmost care. The samples prepared in this way were loaded onto to the test plate of the DMA. The dimensions of every sample were measured by an electronic digital caliper (PRO-MAX, Fowler, USA) which had precision of ±0.01 mm.

2.3. X-ray diffraction (XRD) measurement

The maize seeds with different moisture content (11.9%, 14.6%, 16.4%, 20.7%, 23%, 25.9%, w/w) were ground into powders by a grinder. Then the diffraction patterns of these powders were determined using an X-ray diffractometer (XD-2, Beijing Purkinje General Instrument Co., Ltd., China). It worked at a current of 20 mA and voltage of 36 kV and used Nickel filtered Cu $K\alpha$ radiation (λ = 0.15406 nm). The slit width of 1° and the 2θ range from 5° to 60° in steps of 0.02° per second were used.

2.4. Scanning electron microscopy (SEM)

The surface morphology of cut section of the seeds equilibrated to different relative humidity values was examined using a scanning electron microscope (JSM-5800, JEOL, Japan). The sample were placed and dispersed on top of a circular platform and then plated with gold. All the samples were examined at 400× and 1000× magnifications using an accelerating voltage of 15 kV.

2.5. Dynamic mechanical analysis

The mechanical characteristic of the maize seed was determined using a dynamic mechanical analyzer (DMA, Q800, TA Instruments, New Castle, USA). All the tests were conducted in compression mode. All necessary instrumental calibrations were performed before these tests following the operation manual (TA Instruments, 2004). For all DMA measurements, a 0.01 N preload was applied to ensure that the sample was adequately contacted by both the plates.

2.5.1. Creep analysis

It has been mentioned by Menard (1999a) that repeating the mechanical creep-recovery test can provide better insight into the real-life creep behavior of materials. Hence, the creep-recovery cycle was repeated three times to observe the mechanical characteristics of the maize seeds when they were subjected to repeated stress. A constant stress was applied to the maize seed and the corresponding strain was measured as a function of time. The applied stress was subsequently removed and the strain recovery was measured. The creep time and the recovery time were set at 5 min each in these experiments and the stress was set at 0.02 MPa. All these tests were carried out in triplicate.

2.5.2. Stress-relaxation analysis

The materials having different relaxation behavior exhibit different viscoelastic properties. The ideally viscous samples show an instantaneous relaxation and ideally elastic samples do not relax. In viscoelastic fluids the residual stress relaxes to zero. In the case of viscoelastic solids, their stress relaxes gradually and ultimately approaches an equilibrium stress value greater than zero (Menard, 1999a; Steffe, 1992).

The 3-element [Eq. (1)] and 5-element [Eq. (2)] Maxwell model were used to predict the stress relaxation behavior of the maize seeds.

$$P = E_1 \exp\left(-\frac{t}{\tau_1}\right) + E_c \quad (1)$$

$$P = E_1 \exp\left(-\frac{t}{\tau_1}\right) + E_2 \exp\left(-\frac{t}{\tau_2}\right) + E_c \quad (2)$$

where $P(t)$ represents the relaxed stress (MPa) at any time, E_1 and E_2 (MPa) represent the elastic modulus for each Maxwell component respectively, τ_1 and τ_2 (s) represent the relaxation times, E_c (MPa) represents the equilibrium elastic modulus.

A constant strain was applied to the maize seed and the corresponding stress was measured as a function of time in these stress relaxation tests. The maize seed was held at a constant strain of 0.8% for 10 min in the compression mode. All the relaxation tests were also replicated three times.

2.5.3. Temperature sweep tests

The temperature sweep tests were carried out using compression clamps at a constant strain of 0.8% (within liner elastic limits). The test temperature was increased from 25 °C to120 °C at a heating rate of 3 °C/min with frequency of 1 Hz. The temperature sweep tests were repeated at least three times.

2.5.4. Frequency sweep tests

The frequency of vibration of the agricultural products in the production line or the transportation vehicles ranges from about 1 to 50 Hz (Li et al., 2010). By scanning across the frequency range (0.1–50 Hz) and keeping strain and temperature unchanged, the frequency sweep tests were conducted. The frequency range was set at 0.1–50 Hz and the strain was kept 0.8% in all these tests. All these frequency sweep tests were replicated more than three times.

2.6. Statistical analysis

The results obtained from the creep, stress-relaxation and frequency sweep tests were analyzed using TA Instrument's Universal Analysis 2000 Software Version4.3A (TA Instruments, USA). The creep and stress-relaxation data were modeled according to 4-element Burgers model and Maxwell model, respectively. The non-linear regression feature of SPSS 17.0 (SPSS Inc., Chicago, USA) software was used for this purpose. Values were reported in mean ± standard deviation ($n = 3$). Duncan-test was used to determine the significance when necessary at 95% confidence level ($p < 0.05$).

3. Results and discussion

3.1. Morphology of cut section of maize seeds

Fig. 1 shows the SEM morphology of cut section of maize seeds at moisture contents of 11.9% (Panels A and B), 14.6% (Panels C and D), 16.4% (Panels E and F), 20.7% (Panels G and H), 23% (Panels I and J), 25.9% (Panels K and L). From Panels B, D, F, H and J, it can be seen that the increase in the moisture content causes expansion of the cellular structure of the maize seeds which is perhaps due to the increase in the degree of hydration.

3.2. X-ray powder diffraction analysis

The X-ray diffraction patterns of maize seeds with different moisture contents between 5° (2θ) and 60° (2θ) are shown in Fig. 2. As can be seen from Fig. 2(A)–(F), the characteristic peaks at about 14.0°, 16.0°, 16.8° and 22.0° (2θ) indicate that the crystalline structure of maize seeds shows A type pattern. Two single peaks at about 14.0° and 22.0° (2θ), a dual-peak at 16.0° and 16.8° were observed in the X-ray diffraction pattern. The values of peak intensity at 22.0° (2θ) were the highest, followed by those at 16.0° and 16.8° (2θ), and the lowest at 14.0° (2θ). This diffraction pattern is similar to XRD pattern of corn starch with the diffraction peaks at 15°, 17°, 18°, 23° (Chi et al., 2008). The similarity in the diffraction peaks of maize seed powder to that of maize starch is due to the fact that the crystalline fraction in maize seed comes from its starch content.

3.3. Creep analysis and modeling

In a creep test, a constant stress is applied to a sample and the corresponding strain is measured as a function of time. The creep curve can be seen as the sum of the instantaneous elastic deformation, retarded elastic deformation and viscous flow deformation. The creep deformation curves consist of three regions. The first region is represented by the spring unit of the Maxwell element which shows the initiation of elastic deformation in a very short time frame known as the instantaneous elastic deformation. The second region is represented by the Kelvin–Voigt element which indicates the retarded elastic deformation. The third region is represented by the dashpot of the Maxwell element which indicates the strain recovery after the external force is removed and is known as the viscous flow deformation (Steffe, 1992).

The creep behavior can be described by a 4-element Burgers model (Chuang & Yeh, 2006) represented by Eq. (3).

$$\varepsilon = \frac{\sigma}{E_0} + \frac{\sigma}{E_r}\left(1 - \exp\left(-\frac{t}{\tau_r}\right)\right) + \frac{\sigma}{\eta}t \quad (3)$$

where, ε (dimensionless) is the total strain at any time t and t is the time of the creep test (s). σ (MPa) is the applied stress, E_0 (MPa) is the instantaneous elastic modulus, E_r (MPa) is the retarded elastic modulus, τ_r (s) is the retardation time of the Kelvin component, η (MPa s) is the viscous component of the dashpot.

The parameters (E_0, E_r, τ_r and η) in Eq. (3) were obtained from the strain-time curves of the three measurements using nonlinear regression analysis and are presented in Table 1.

Fig. 3 shows the ε(%) as a function of time for maize seeds within a moisture content range of 11.9% to 25.9% (w/w). As can be seen from this figure that the magnitude of the creep (ε%) increased when the moisture content increased. The reason for this observation will be explained shortly.

It can be seen from Table 1 that all the regression parameters have the coefficient of determination (R^2) > 0.97. This observation suggests that the 4-element Burgers model can represent the creep behavior of maize seed well. The tabulated values also show that the values of E_0, E_r, η decreased as the moisture content increased. In the case of τ_r, it decreased when the moisture content increased from 11.9% to 20.7% (w/w) while it remained almost constant within 23% to 25.9% (w/w). There was no significant difference ($p > 0.05$) between τ_r of each cycle when the moisture content varied from 11.9% to 23% (w/w). However, the variation in the τ_r among the cycles was significant ($p < 0.05$) at the latter two moisture contents. E_0 and E_r represent the elasticity and hardness of the test material. If the values of E_0 and E_r are small, the height of the

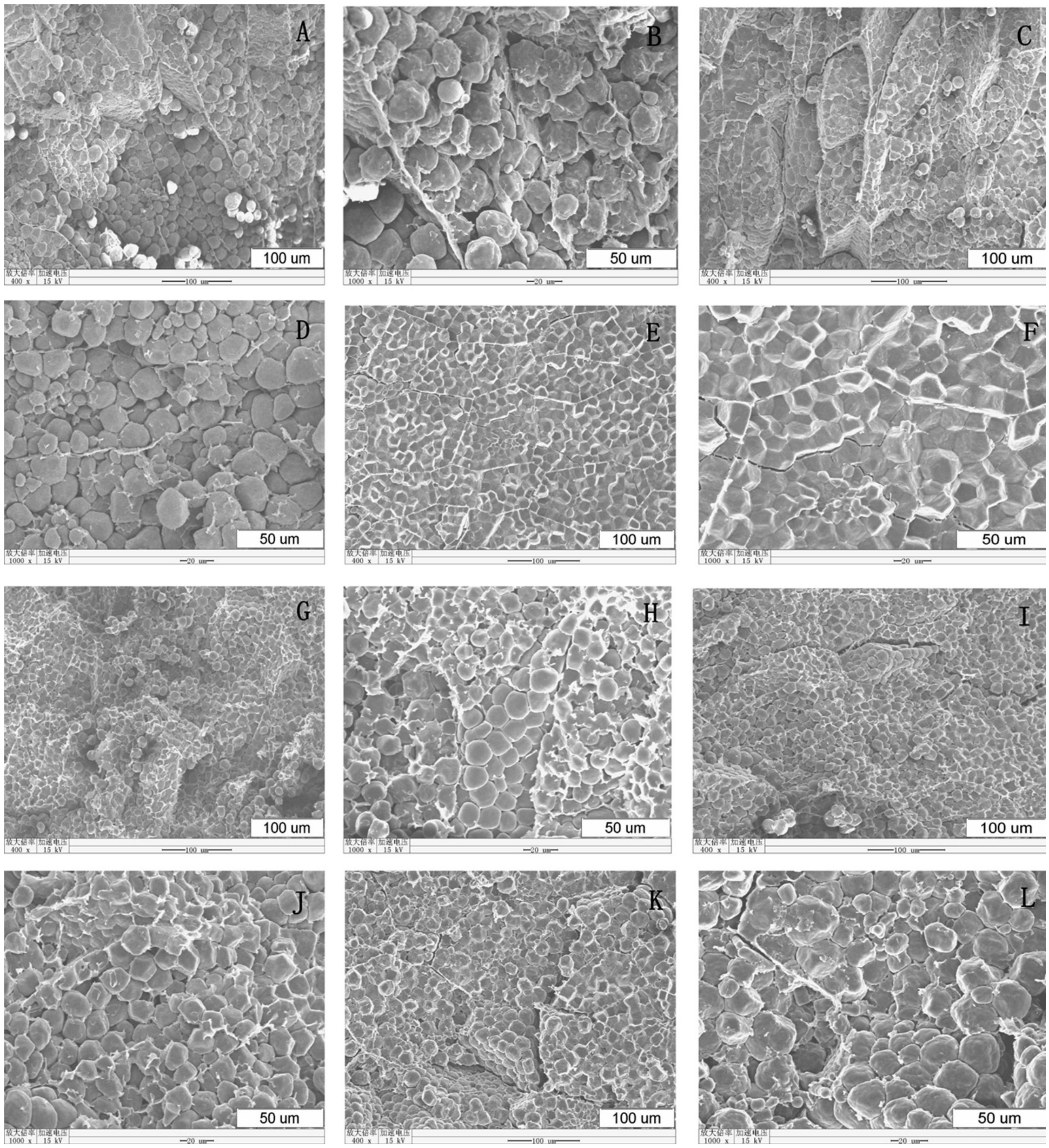

Fig. 1. SEM microphotographs of cut section of maize seeds with different moisture content (11.9–25.9%).

creep curve will increase. Therefore, the height of the creep curve (ε%) increased as the moisture increased (Fig. 3).

At 14.6% (w/w) moisture content, the values of E_r and η were significantly differed with each other ($p < 0.05$). At 16.4% (w/w) moisture content, the values of η obtained from different cycles differed from each other significantly ($p < 0.05$). At 20.7% (w/w) moisture content, there was significant difference between the parameter E_r of the first and the third cycle. At 23% and 25.9% (w/w) moisture contents, significant difference was observed in E_0 and η values between the first cycle and the latter two cycles. E_0 (MPa) is the instantaneous elastic modulus, E_r (MPa) is the retarded elastic modulus, τ_r (s) is the retardation time of the Kelvin component, η (MPa s) is the viscous component of the dashpot. E_0 and E_r represent the elasticity and hardness of the test material. Because maize kernel is a kind of viscoelastic material, there is deformation that can not be recovered called residual deformation in each cycle. At 14.6% (w/w) moisture content, large deformation occurs in the first and second cycle. At 16.4% (w/w) moisture content, large deformation occurs in the first and second cycle. At 20.7% (w/w) moisture content, small deformation occurs in the first and second cycle. At 23% and 25.9% (w/w) moisture contents, large deformation occurs in the first cycle and small deformation occurs in the second cycle.

3.4. Stress-relaxation analysis and modeling

Fig. 4 shows the values of the stress $E(t)$, as a function of time for maize seeds within the moisture content range of 11.9% to 25.9%. As can be seen from this figure, the magnitude of the relaxation curves ($E(t)$ values) decreased as the moisture content increased. These stress relaxation curves consist of two regions. The first region which has high $E(t)$ values for a short time indicates to the short-time response while the second region having relatively lower $E(t)$ values for longer duration indicates to the long-time response.

As shown in Fig. 4, the stress of maize seed sample relaxed gradually and finally reached an equilibrium value indicating that this is viscoelastic in nature.

It can be seen from the equations above that there is one relaxation time (τ_1) in the 3-element Maxwell model [Eq. (1)], but there

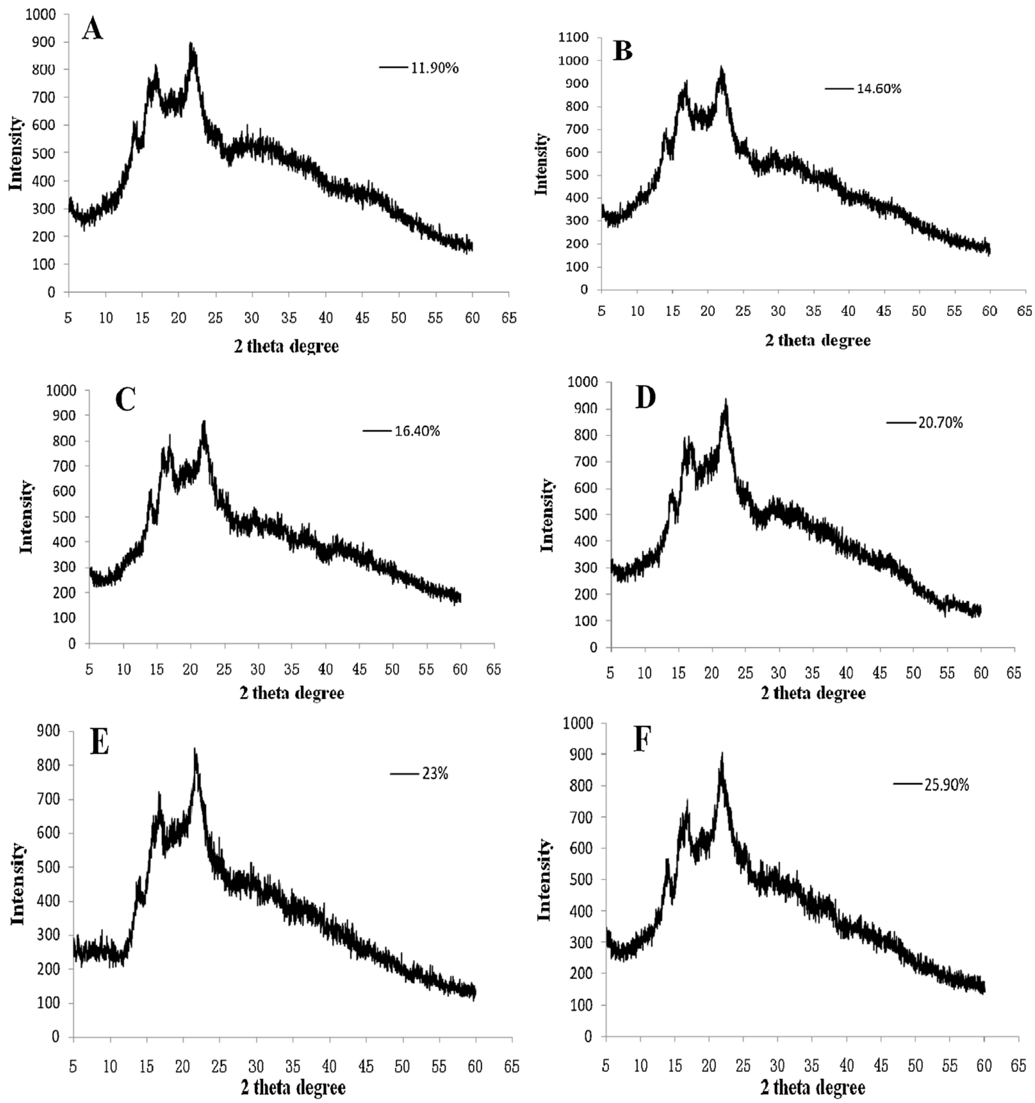

Fig. 2. X-ray diffraction patterns of maize seeds with different moisture contents (11.9–25.9%).

Table 1
The parameters of the Burgers model representing the creep behavior of the maize seeds⁺.

Moisture content (%)		E_0 (MPa)	E_r (MPa)	τ_r (s)	η (MPa s)	R^2
11.9	Cycle1	0.033 ± 0.002^{a}	0.241 ± 0.022^{a}	11.915 ± 3.423^{a}	37.053 ± 7.347^{a}	0.992
	Cycle2	0.050 ± 0.006^{b}	0.441 ± 0.081^{b}	11.073 ± 1.475^{a}	56.957 ± 10.482^{a,b}	0.993
	Cycle3	0.054 ± 0.010^{b}	0.527 ± 0.133^{b}	10.198 ± 0.956^{a}	71.427 ± 13.284^{b}	0.993
14.6	Cycle1	0.021 ± 0.002^{a}	0.180 ± 0.025^{a}	9.168 ± 1.536^{a}	33.412 ± 4.763^{a}	0.987
	Cycle2	0.039 ± 0.005^{b}	0.384 ± 0.044^{b}	9.532 ± 1.562^{a}	53.031 ± 3.710^{b}	0.993
	Cycle3	0.045 ± 0.005^{b}	0.484 ± 0.046^{c}	9.283 ± 0.852^{a}	66.919 ± 3.270^{c}	0.992
16.4	Cycle1	0.018 ± 0.002^{a}	0.145 ± 0.011^{a}	9.050 ± 1.703^{a}	32.005 ± 0.140^{a}	0.985
	Cycle2	0.032 ± 0.005^{b}	0.306 ± 0.066^{b}	9.710 ± 0.201^{a}	51.932 ± 2.550^{b}	0.990
	Cycle3	0.037 ± 0.007^{b}	0.391 ± 0.100^{b}	8.745 ± 0.631^{a}	64.041 ± 5.494^{c}	0.989
20.7	Cycle1	0.014 ± 0.001^{a}	0.168 ± 0.030^{a}	8.186 ± 1.544^{a}	38.644 ± 18.692^{a}	0.983
	Cycle2	0.018 ± 0.002^{b}	0.254 ± 0.047^{a,b}	7.224 ± 1.348^{a}	49.151 ± 19.501^{a}	0.987
	Cycle3	0.020 ± 0.002^{b}	0.293 ± 0.050^{b}	7.236 ± 1.246^{a}	52.109 ± 15.722^{a}	0.988
23	Cycle1	0.010 ± 0.001^{a}	0.074 ± 0.019^{a}	8.174 ± 1.480^{a}	26.821 ± 1.244^{a}	0.975
	Cycle2	0.017 ± 0.004^{b}	0.122 ± 0.057^{a}	8.517 ± 0.667^{a}	33.967 ± 3.125^{b}	0.982
	Cycle3	0.019 ± 0.004^{b}	0.140 ± 0.072^{a}	8.565 ± 1.064^{a}	33.888 ± 4.516^{b}	0.985
25.9	Cycle1	0.010 ± 0.001^{a}	0.055 ± 0.003^{a}	9.447 ± 0.373^{a}	23.173 ± 3.223^{a}	0.975
	Cycle2	0.012 ± 0.002^{a}	0.063 ± 0.003^{b}	8.040 ± 0.091^{b}	27.549 ± 3.605^{a}	0.975
	Cycle3	0.012 ± 0.001^{a}	0.066 ± 0.003^{b}	7.531 ± 0.560^{b}	24.524 ± 1.047^{a}	0.979

⁺Values represent the mean ± standard deviation of triplicate tests.
⁺Values of the same moisture content in a column with different superscripts were significantly different ($p < 0.05$).

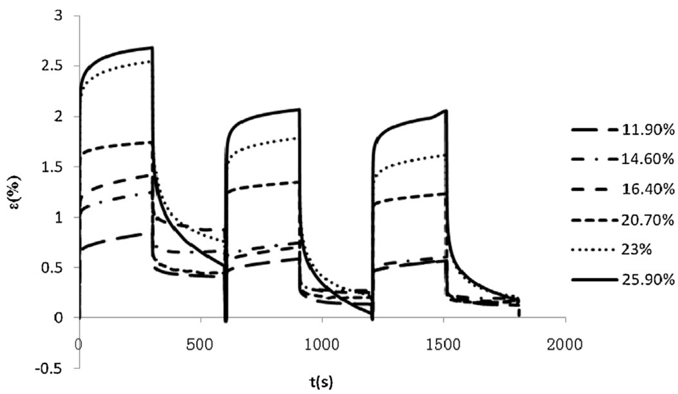

Fig. 3. The $\varepsilon(\%)$ as a function of time for maize seed having moisture contents from 11.9 to 25.9%.

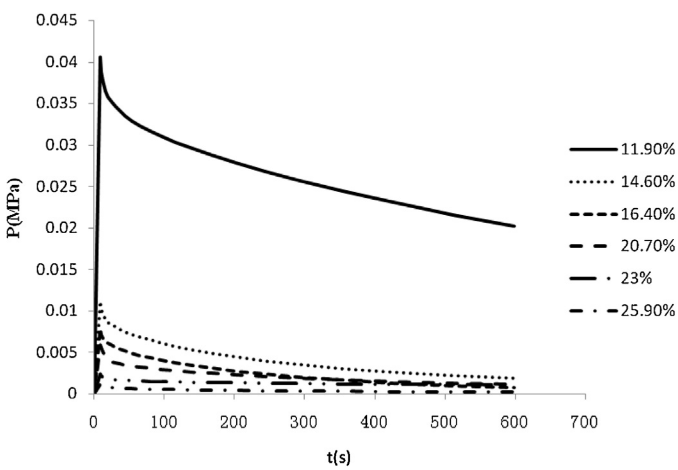

Fig. 4. The stress, $E(t)$, as a function of time for maize seed in the moisture content range of 11.9–25.9%.

are two relaxation times (τ_1 and τ_2) in the 5-element Maxwell model [Eq. (2)]. As mentioned above, the stress relaxation curve of maize seed has two regions having a short-time response and a long-time response. The presence of two relaxation regions means that the 5-element Maxwell model should be able to better represent the relaxation behavior of maize seeds than the 3-element model.

The relaxation parameters (E_1, E_2, E_c, τ_1 and τ_2) were obtained from the stress-time curves through nonlinear regression. The parameters of both the 3-element and 5-elmement Maxwell models are presented in Table 2.

It can be seen from Table 2 that the values of E_c, E_1 and τ_1 decreased as the moisture content increased from 11.9% to 25.9% (w/w). A similar trend was observed in the case of 5-element model that the values of E_1, E_2, E_c, τ_1, τ_2 decreased with increase in moisture content within the moisture content range tested.

The value of the relaxation time in the 3-element model monotonously decreased with the increase in the moisture content (202 s at 11.9% and 53 s at 25.9%, w/w). At the same time, the value of the τ_2 in the 5-element Maxwell model monotonously decreased with increase in the moisture content while there was no definite trend in the variation of τ_1 with increase in moisture content.

The R^2 value of the 5-element model at each moisture content value is greater than those of the 3-element model suggesting that the 5-element model better represents the stress relaxation behavior of maize seeds.

3.5. Temperature sweep analysis

The variation of loss modulus (G'') and the tanδ as a function of temperature within the tested moisture content range is presented in Fig. 5. As can be seen the data presented in this figure, tanδ values increased very slowly in the beginning and then increased rapidly until they reached the respective peak values. The values of tanδ decreased after reaching the peak values. The tanδ values at higher temperatures were always higher than at lower temperatures. The trend of variation of G' with temperature was similar to that of tanδ. A notable difference in the variation of tanδ and G'' with temperature was that the peak G'' value always occurred at lower temperatures (shorter times) compared to the peak value of tanδ (Fig. 5).

The reason for appearing of peak G'' at lower temperature than the tanδ can be given by the following mathematical treatment. Assuming that the peak of loss modulus G'' occurred at $T = T_1$, Therefore,

$$\frac{d(\tan\delta)}{dT} = \frac{d}{dT}\left(\frac{G''}{G'}\right) = \frac{\left(\frac{dG''}{dT}\right)G' - G''\left(\frac{dG'}{dT}\right)}{G' \times G'} \quad (4)$$

$$\text{As,} \quad \left.\frac{dG''}{dT}\right|_{T=T_1} = 0, \quad \left.\frac{dG'}{dT}\right|_{T=T_1} < 0 \quad (5)$$

$$\text{So,} \quad \left.\frac{d(\tan\delta)}{dT}\right|_{T=T_1} > 0 \quad (6)$$

Eq (6) indicates that tanδ is still rising at the temperature $T = T_1$. It is expected that the maximum value of tanδ would be attained at temperature $T = T_2$ ($T_2 > T_1$). When the corn seed was heated from 25 °C to 120 °C at a rate of 3 °C/min maintaining 1 Hz frequency, the relaxation process in the seed was clearly observed. This means that specific molecular motions that bring about the relaxation occur in this condition. It is assumed that maize starch is responsible for

Table 2
The stress-relaxation parameters of maize seeds obtained from DMA in compression mode+.

Moisture content (%)		E_c (10^{-3} MPa)	E_1 (10^{-3} MPa)	τ_1 (s)	E_2 (10^{-3} MPa)	τ_2 (s)	R^2
11.9	3-Element model	18.000 ± 2.650	20.000 ± 3.610	202.314 ± 17.118			0.969
	5-Element model	12.700 ± 2.520	5.670 ± 0.577	10.953 ± 1.897	22.000 ± 4.360	413.594 ± 28.854	0.999
14.6	3-Element model	1.330 ± 0.577	8.000 ± 1.000	115.726 ± 22.816			0.971
	5-Element model	3.000 ± 0.100	2.670 ± 0.577	6.739 ± 0.877	7.670 ± 1.160	181.660 ± 31.701	0.999
16.4	3-Element model	1.330 ± 0.577	5.330 ± 0.577	112.666 ± 23.113			0.963
	5-Element model	0.733 ± 0.252	1.930 ± 0.404	6.005 ± 1.404	4.970 ± 0.351	185.963 ± 25.760	0.998
20.7	3-Element model	2.330 ± 0.577	2.900 ± 0.173	79.405 ± 4.267			0.948
	5-Element model	2.000 ± 1.000	1.770 ± 0.252	5.751 ± 2.315	2.330 ± 0.577	169.761 ± 28.491	0.999
23	3-Element model	1.000 ± 0.100	1.330 ± 0.577	64.257 ± 9.929			0.902
	5-Element model	1.330 ± 0.577	1.070 ± 0.208	4.571 ± 0.669	1.170 ± 0.153	145.784 ± 39.157	0.995
25.9	3-Element model	0.300 ± 0.020	0.967 ± 0.153	53.147 ± 4.841			0.931
	5-Element model	0.777 ± 0.106	0.430 ± 0.080	6.818 ± 2.282	0.867 ± 0.153	140.792 ± 23.216	0.999

+Values represent the mean ± standard deviation of triplicate tests.

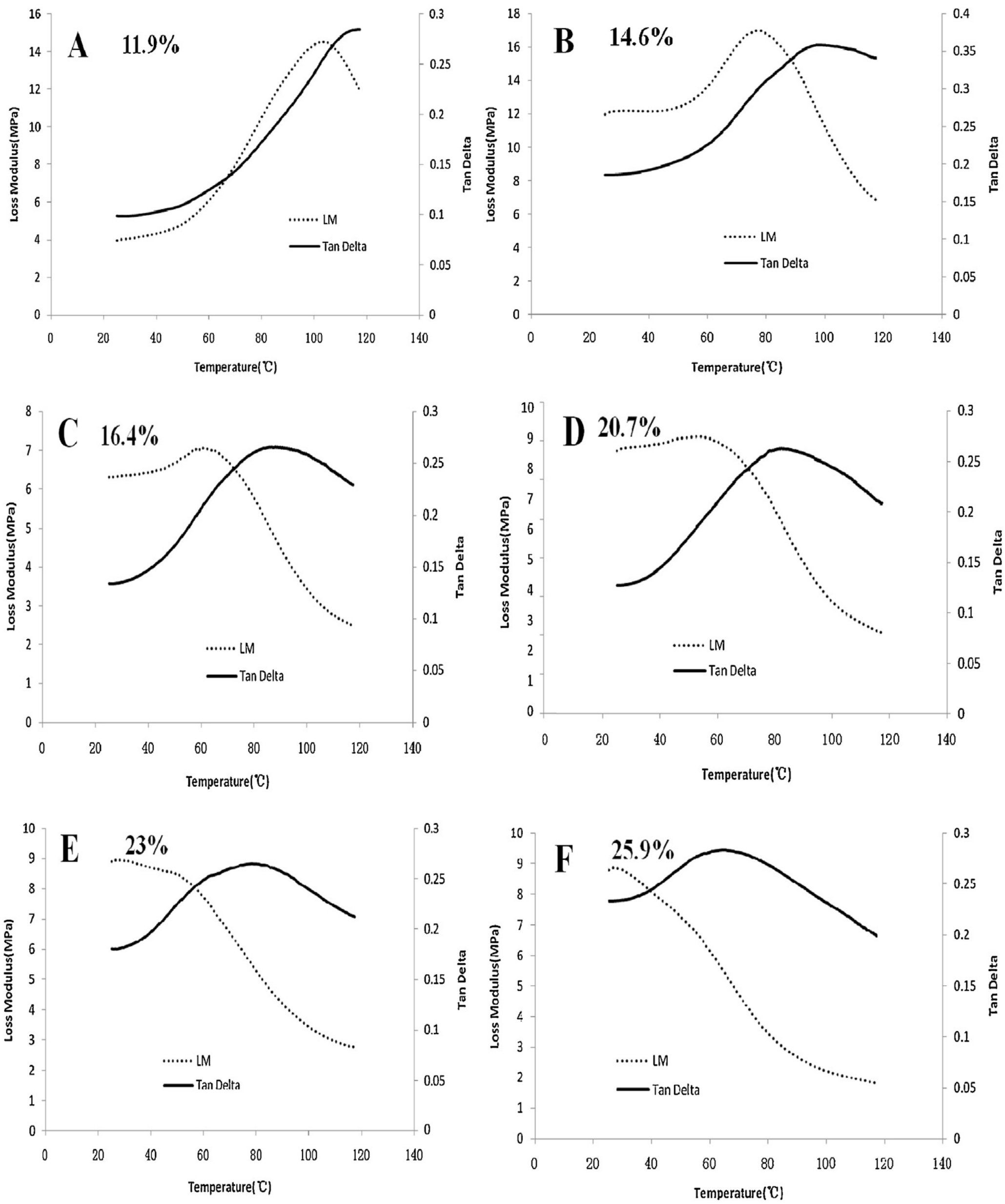

Fig. 5. The loss modulus and the tan delta against temperature curves for the maize seeds with different moisture contents (11.9–25.9%).

this relaxation as large proportion (up to 70%) of the corn seed dry matter comprised of starch. The maize starch comprises macromolecules such as amylose and amylopectin and that the molecular motion of these polymer chains is frozen at ambient or moderate temperatures. When the temperature increases, the molecular motion increases accordingly and the molecules can slide against one another as the polymer becomes flexible when required thermal energy is supplied. Such a physical transition from random or immobilized conformation to a flexible confirmation is called the glass transition. The mechanical glass transition temperature (T_g) can be defined as the temperature at which the maximum tanδ occurs or the inflexion point at which an obvious drop of the storage modulus occurs (Chen et al., 2007). We have taken the peak value of tanδ to be the mean T_g of corn seed. The T_g values for the maize seeds at the moisture contents of 11.9%, 14.6%, 16.4%, 20.7%, 23%, 25.9% were 114 °C, 96 °C, 86 °C, 82 °C, 78 °C, 65 °C respectively. These values are very close to the T_g values corn kernel reported by Hundal and Takhar (2009).

3.6. Frequency sweep analysis

The variation of elastic modulus (G′), G'' and tanδ as a function of frequency within the moisture content range (11.9–25.9%) is shown in Fig. 6. As can be seen from this figure the magnitude of G', G'' and tanδ increased as the frequency increased. The highest G' value in the lower frequency range (0.1 Hz to 19 Hz) was observed at the moisture content value of 16.4% (w/w). The highest G' value was at higher frequency range >19 Hz) was observed at the moisture content value of 20.7% (w/w). The lowest G' was observed at the lowest moisture content (11.9%, w/w) value within the entire frequency range tested. The highest and lowest G'' values were observed at moisture content values of 20.7% of 11.9% (w/w), respectively within the entire frequency range. As can be seen from the frequency dependence of G' and G'' data that the frequency dependence of both G' and G'' is exceptionally high at 20.7% compared to other moisture contents. As can be seen from Fig. 6, the trend in variation of tanδ with moisture content is the mirror image

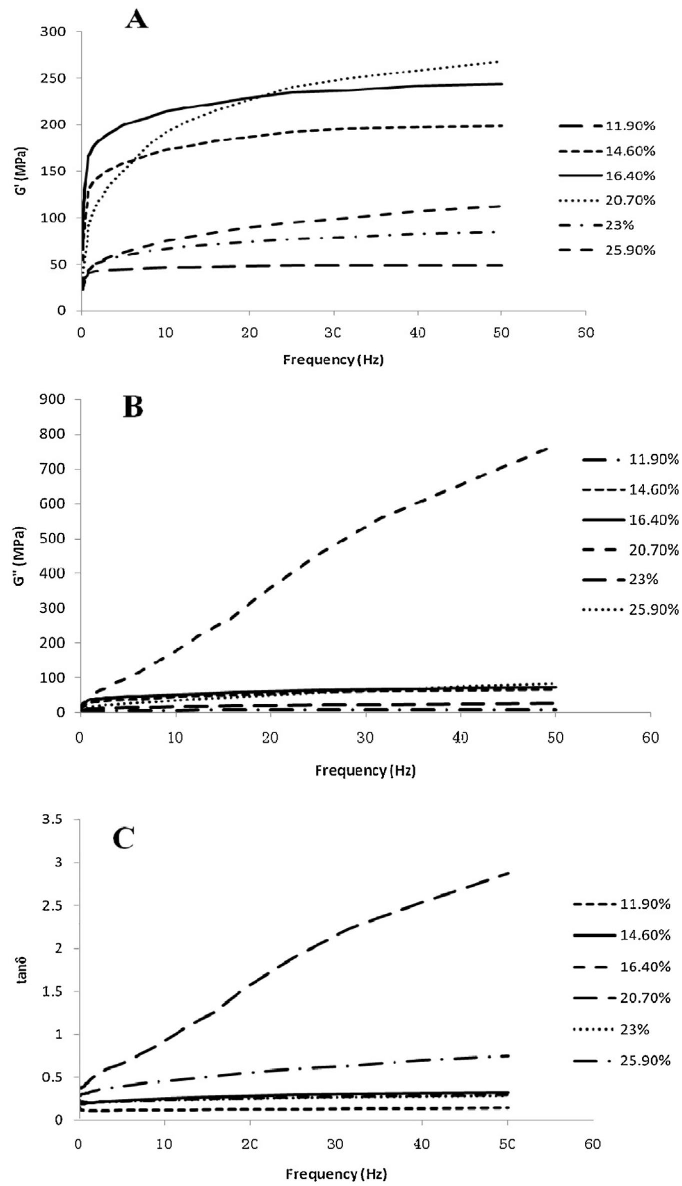

Fig. 6. The variation of elastic modulus (G'), loss modulus (G'' and tanδ as a function of frequency in the moisture content range of 11.9–25.9% (w/w).

of that of G'' and that the value of tanδ is highest at 20.7% (w/w) and lowest at 11.9% (w/w) within the entire frequency range tested. The rate of change of tanδ with frequency was also exceptionally high at the moisture content value of 20.7%. The very high G'' and tanδ values at 20.7% moisture content reflect the very strong of moisture content on the viscous component of maize kernel.

4. Conclusions

We studied the viscoelastic behavior (creep, stress relaxation, temperature and frequency dependence of loss and viscous moduli and loss tangent) of maize kernel together with its morphology (SEM) and X-ray diffraction patterns. The increased in the moisture content and the hydration were found to expand the kernel's cellular structure (SEM). The X-ray diffraction pattern of the maize powder was identical to that of maize starch (type A crystalline pattern) due to dominance of crystalline corn starch in the kernel structure. The maize corn behaved as viscoelastic material under mechanical compression. The 4-element Burgers model was found to adequately represent the creep behavior of the maize seeds ($R^2 > 0.97$). The 5-element Maxwell model was able to better predict the stress relaxation behavior of maize seed better than the 3-element Maxwell model. For the 5-element [Eq. (2)] Maxwell model, $P(t)$ represents the relaxed stress (MPa) at any time, E_1 and E_2 (MPa) represent the elastic modulus for each Maxwell component respectively, τ_1 and τ_2 (s) represent the relaxation times, E_c (MPa) represents the equilibrium elastic modulus. The relaxation time equals to the time taken by the stress decreasing to 36.8% of the initial stress. There is one relaxation time (τ_1) in the 3-element Maxwell model [Eq. (1)], but there are two relaxation times (τ_1 and τ_2) in the 5-element Maxwell model [Eq. (2)]. As mentioned above, the stress relaxation curve of maize seed has two regions having a short-time response and a long-time response. The presence of two relaxation regions means that the 5-element Maxwell model is able to better represent the relaxation behavior of maize seeds than the 3-element model. The magnitude the creep strain was found to increase as the moisture content of the sample increased. The magnitude of the relaxation stress was found to decrease as the moisture content increased. The T_g values for the maize kernels decreased with increased moisture content. For example, the T_g values were 114 °C and 65 °C at moisture content values of 11.9% (w/w) and 25.9% (w/w), respectively. The magnitude of the loss moduli and loss tangent and their rate of change with frequency were highest at 20.7% and lowest at 11.9% moisture contents.

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