

GLASS TRANSITIONS IN STARCH, GLUTEN AND BREAD AS MEASURED

Dielectric spectroscopy and TMA methods

V. T. Huang^{**}, L. Haynes^{*1}, H. Levine and L. Slade^{*}

^{*}Nabisco Foods Group, East Hanover, NJ 07936

^{**}The Pillsbury Company, Minneapolis, MN 55414, USA

Abstract

Dielectric Spectroscopy (DS) and Thermomechanical Analysis (TMA) were used to identify the glass transition temperature (T_g) of native wheat starch, vital wheat gluten and a commercial bread, in response to changes in moisture content. An open-ended coaxial probe technique was used to measure the permittivity or dielectric constant (ϵ') and the loss factor (ϵ'') as functions of moisture, for 2.45 GHz frequency, at constant density and temperature. Plots of ϵ' and ϵ'' as functions of moisture content showed dramatic changes in mobility-based dielectric properties, which occur upon transition from the glassy solid to the rubbery liquid state. The modified TMA method can measure the change in viscoelastic properties around T_g . This study further confirms that synthetic polymer science principles can be applied to food systems.

Keywords: bread, dielectric spectroscopy, glass transition, gluten, starch, TMA

Introduction

Permittivity, ϵ' , of foods is almost exclusively defined by water content and its interaction with other components in foods (i.e. protein, starch, etc.) [1]. Gluten and starch, two major polymer components of wheat flour-based foods, when hydrated with water (i.e. plasticized), become soft, deformable, but resistant to rupture. This is an important functional characteristic relied upon by manufacturers of baked goods [2]. Identification of T_g , in response to changes in temperature and/or moisture content of starch and gluten polymers, by means of dielectric spectroscopy offers a unique opportunity to observe T_g through dipole relaxation in the microwave frequency timeframe (i.e. nanoseconds).

A limited amount of information is available on the dielectric properties of a complex food system such as bread. One study, involving measurement of the dielectric properties of Pillsbury Pip-pin HotTM dough, showed variation in the dielectric permittivity with variations in water and flour content [3]. In another

1 Author to whom all correspondence should be addressed.

study, the dielectric properties of starch–gluten–water mixtures were found to be dependent upon the ratio of starch to gluten, as well as dependent upon moisture content [4]. In a third study, the dielectric properties of granular and gelatinized starch–water mixtures were measured at 1 and 3 GHz over a wide compositional range [5–7]. This study showed that as the proportion of carbohydrate to water increased, there was a consequent decrease in permittivity of the mixture. More recently, the dielectric permittivity and relaxation time for cracker dough, starch and gluten were identified [8]. Dipole relaxation times were related to moisture content and to the existence of free water.

T_g of starch and gluten have been determined by mechanical methods, such as TMA [9, 10], Dynamic Mechanical Thermal Analysis (DMTA) [11–13], and mechanical acoustic methods [14]. TMA has been used to study the phase transitions of granular starch [15]. A two-stage swelling pattern was observed with hydrated starch (50% starch), which the authors attributed to the glass transition of the amorphous phase and to the melting of crystallites. Bread has been studied by modified TMA [16] and DMTA [17].

The purpose of the present study was to measure the dielectric properties, ϵ' and ϵ'' , of native wheat starch, gluten and bread, at 2450 MHz, as functions of moisture content. As the moisture contents of gluten, starch and bread were increased, T_g became observable by a significant increase in permittivity, reflecting the increased molecular mobility of the responding dipole. An open-ended coaxial probe technique was used to obtain spectral data [18]. Dielectric properties were measured at constant temperature and density. Achievement of the latter was important to isolate changes in ϵ'' resulting from mobility of the polymer, only. Another objective was to determine the T_g curves of gluten and starch by a modified TMA method [16]. The TMA instrument was modified to include an oscillating load, in order to detect changes in both dimensions and mechanical properties of the sample. Results are representative of the physical changes in the hydrated gluten and starch. The moisture range covered was from 0 to 40% moisture content (weight basis).

Materials and methods

Preparation of starch, gluten and bread samples

White bread crumb (WonderTM), native wheat starch (Sigma Chemical Co., St. Louis, MO) and vital wheat gluten (Ogilvie Mills, Montreal, Canada), in the moisture range of about 20 to 40%, were hydrated to a predetermined moisture using the 'work free dough' method [19]. Moisture contents of 'as is' starch and gluten were measured. Wonder Bread was freeze-dried, then rehydrated. The 'as is' moisture was determined; this amount was subtracted from the weight of water required to hydrate the sample to a target moisture. Target mois-

tures ranged from 20 to 40%. The amount of water required to hydrate 8.5 g of sample to target moisture was weighed into a plastic tube, frozen in liquid N₂, then milled in a Spex model 6700 freezer mill for 1 minute. Gluten, with an initial moisture content of 7.5%, required 2.5, 3.0 and 7.1 g of frozen, milled ice to be brought to moisture contents of 26, 28 and 39%, respectively. 8.5 g of starch, with an initial moisture content of 10.4%, required 1.5, 2.9, 3.4 and 4.8 g of frozen, milled ice to be brought to moisture contents of 19, 24, 26 and 38%, respectively. The mixtures were milled for 3 minutes, transferred to a closed container and equilibrated to room temperature overnight. Resulting moisture contents were measured by vacuum oven. Bread, wheat starch and wheat gluten, in the moisture range of 0 to about 19%, were incubated in various constant relative humidity chambers at room temperature for up to 2 weeks.

Moisture measurements

The moisture contents of starch, gluten and bread were measured by drying in a vacuum oven (625 mm Hg) for 18 h at 70°C. The difference in sample weight, before (wet) and after drying, was divided by the 'wet' weight and multiplied by 100 to give % moisture content.

Dielectric permittivity measurements

Complex dielectric permittivity was measured with a Hewlett-Packard open-ended coaxial-line probe, model 85070B, over the range mentioned above, using a Hewlett-Packard model 8752 Network Analyzer. The technique is based on the determination of the phase of the reflection coefficient and is nondestructive. Three dielectric references with well-known dielectric constants are required for calibration. In this work, air, a metal short-circuit, and water were used. The probe used was an open-ended coaxial line having an inner radius 1.0 mm, an outer radius 3.5 mm, and a ground plane flange of 18 mm in diameter. A major source of error in these experiments arises from any air gap that exists between the coaxial probe and the sample surface.

Starch, bread and gluten were prepared for dielectric measurement as described previously [8]. Briefly, samples were packed uniformly into a polypropylene container of either 8 or 16 ml volume. Sample density was adjusted by adjusting the weight of sample in the container. Constant sample densities were used for starch (0.60 g/cc), gluten (0.74 g/cc) and bread (0.43 g/cc). A constant sample temperature of 22°C was chosen. Precaution was taken to avoid surface drying. Three measurements were averaged. From the measurement of the phase of the reflection coefficient, a value for the dielectric constant of the material was determined, based upon accurate determination of the short-circuit, air, and water calibration standards.

TMA procedure

About 0.5 g of sample was packed in a pneumatic press (model 00-25, Beckman Instruments, Inc., San Diego, CA), under 2-6 tons of pressure, to make a 100-mm-diameter pellet with 0.1-0.2 mm thickness. A portion of this pellet was placed in an aluminum pan 6 mm in diameter. Dehydration during a TMA run (below 100°C) was minimized by coating the sample with paraffin oil.

A previously published method was used to measure the changes in sample dimensions and softness for starch, gluten, and bread samples during heating [16]. The TMA was modified as follows. A sinusoidal oscillator, operating at 0.08 Hz, drives a stationary coil that surrounds one end of the Almico rod magnet attached to the top of the TMA aluminum/quartz probe. Current in the coil creates a magnetic field that produces an axial, peak-to-peak, sinusoidal force of 0.5 g. The sample is weight-preloaded, so that the probe always contacts the sample. A flat probe with a diameter of 5 mm was used. The measurement of probe displacement represents changes in sample thickness and probe penetration into the sample. The width of the TMA curve reflects the response of the sample to oscillating stress, i.e. its softness. The onset temperature of softening is defined as T_g .

Results and discussion

Dielectric permittivity

Results of permittivity measurements of bread, gluten and starch, over a frequency range of 0.2 to 20 GHz, are shown in Fig. 1. Plots of ϵ'' and ϵ' as func-

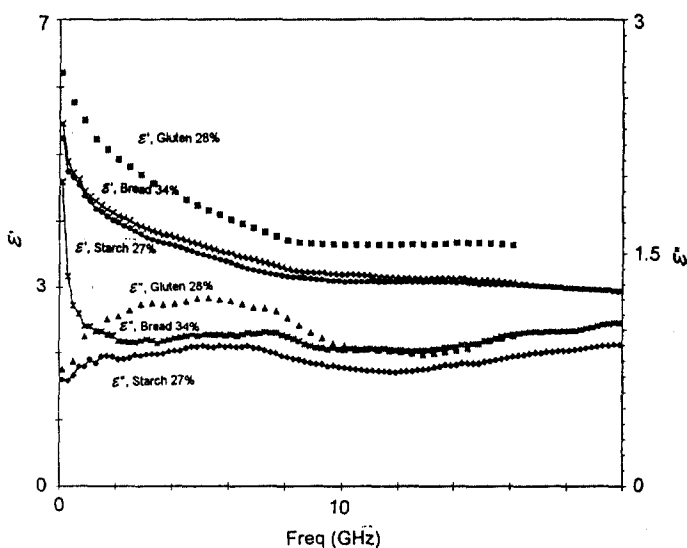


Fig. 1 Effect of frequency on ϵ' and ϵ'' of bread, gluten and starch at 22°C

tions of frequency show the contribution of d.c. conductivity to the measured loss, ϵ'' , for bread at frequencies below 1 GHz. Starch and gluten have little contribution from d.c. conductivity to the measured loss, due to their lack of free salts. For all three materials, the relaxation frequency, f_r , the frequency at which maximum loss occurs (i.e. average dipole response time), is observed over a broad frequency range. Typically, the variation in measured ϵ'' is ± 0.02 .

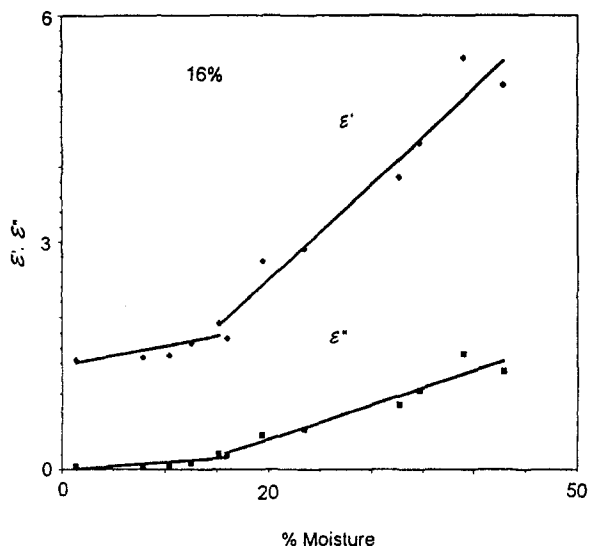


Fig. 2 Effect of moisture content on ϵ' and ϵ'' of bread measured at 2.45 GHz and 22°C (density = 0.43 g cm⁻³)

Figure 2 shows ϵ' and ϵ'' , at 2.45 GHz frequency, as functions of increasing moisture content for bread. A sharp increase in ϵ' and ϵ'' was observed at 16% moisture for bread. Increasing the moisture that plasticizes the polymer matrix sufficiently lowered T_g of the polymer, so that the transition from a glassy solid (at moisture below 16%) to a rubbery liquid (moisture above 16%) could be observed at the temperature of the experiment, 22°C [2].

Figures 3 and 4 shows ϵ' and ϵ'' , at 2.45 GHz frequency, as functions of increasing moisture content for starch and gluten. A sharp increase in ϵ' and ϵ'' was observed at 19 and 25% moisture, respectively. At 22°C, starch with less than 19% moisture is a glassy solid, immobile material with very little dipole response. The same is true for gluten below 22% water content. Gluten was by far the more viscous in its rubbery state above T_g . Dielectric spectroscopy identified a higher moisture content for T_g of gluten at 22°C than did TMA. This could be a result of gluten's extremely viscous nature preventing full mobility of the responding dipoles. Only dipoles of sufficient mobility could be observed by dielectric spectroscopy at microwave frequency and nanosecond timeframe.

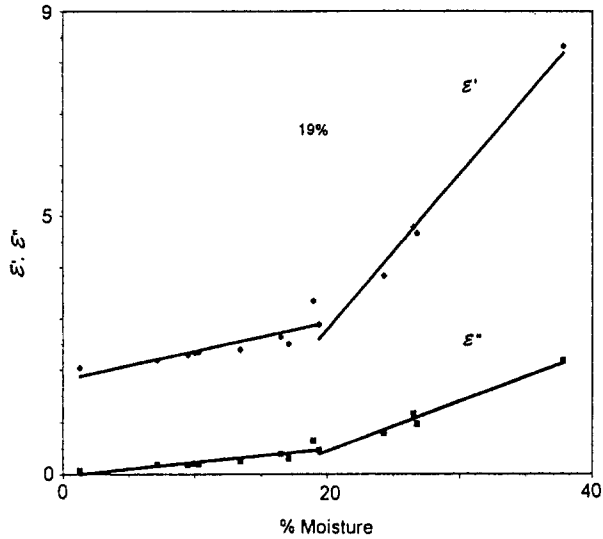


Fig. 3 Effect of moisture content on ϵ' and ϵ'' of starch measured at 2.45 GHz and 22°C (density = 0.60 g cm⁻³)

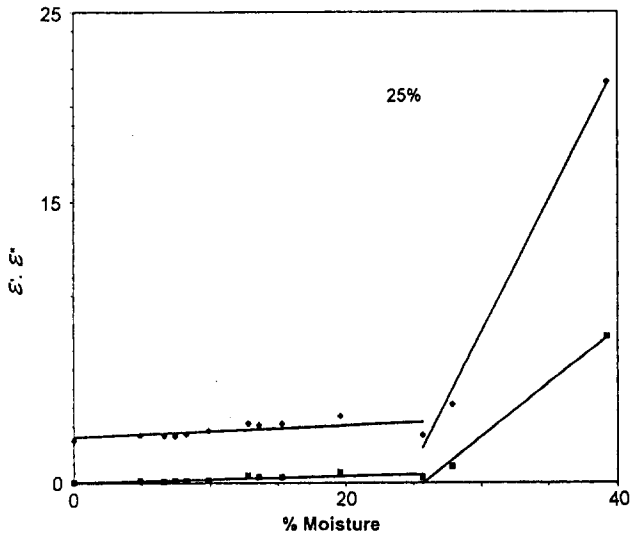


Fig. 4 Effect of moisture content on ϵ' and ϵ'' of gluten measured at 2.45 GHz and 22°C (density = 0.74 g cm⁻³)

T_g determination from TMA curves

In Fig. 5, the upper TMA curve for 25.7%-moisture gluten represents the change in dimensions of the sample as a function of temperature. Changes in the curve thickness reflect changes in softness during heating. The first-order de-

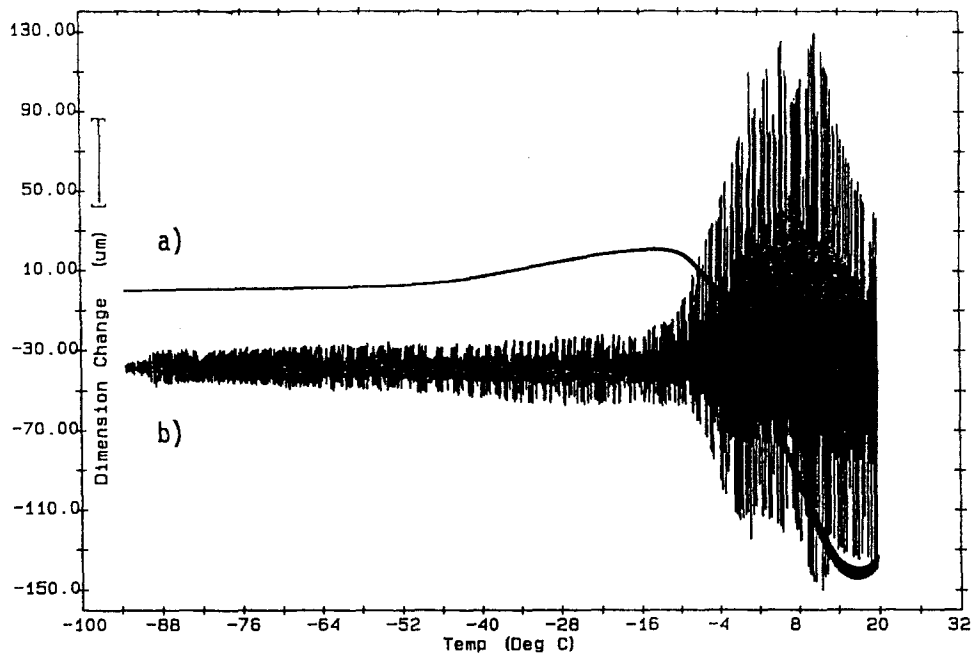


Fig. 5 a) TMA curve for a 25.7%-moisture gluten sample, b) first-order derivative of the TMA curve

ivative is even more sensitive to the change in softness (lower curve), noted by deviation from zero. For gluten with 25.7% moisture, softening was observed to start at -12°C (Fig. 5).

Figures 6, 7 and 8 show the T_g curves of gluten, starch and bread, respectively. A previously published T_g curve for bread, determined by TMA [16], has been shown to be similar to that determined by a DMTA method [11]. The gluten and starch T_g curves are in close agreement with the DMTA results for gluten and amylopectin from Kalichevsky et al. [20, 21]. Figure 6 also shows that the TMA data fit well with literature DSC data for gluten at various moisture contents [22].

The T_g data for native wheat starch are much noisier than those for gluten and bread, especially for high-moisture samples. This was probably due to the presence of starch and/or ice crystallites, whose rigidity would mask the softness change amorphous regions at T_g . This is one of the difficulties associated with TMA measurements [10]. Others are ice melting and moisture loss due to squeezing or evaporation. Pressures of around 2 tons should be applied for high-moisture samples, to avoid squeezing out liquid water. Moisture loss at lower temperatures was minimized by coating samples with paraffin oil. However, at higher temperatures, some moisture loss was inevitable. Kalichevsky *et al.* [20, 21] also reported the same problem, for samples with T_g higher than 90°C , during DMTA measurements.

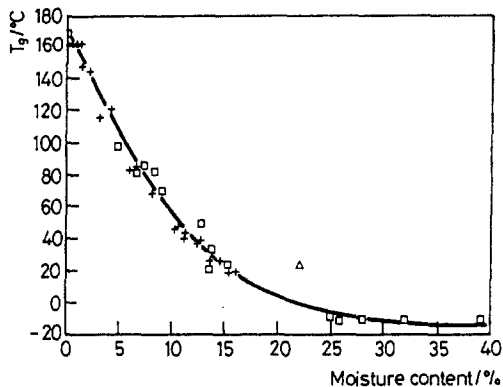


Fig. 6 Effect of moisture content on T_g of gluten (\square TMA data; + DSC data). W_g identified by dielectric spectroscopy is indicated (Δ)

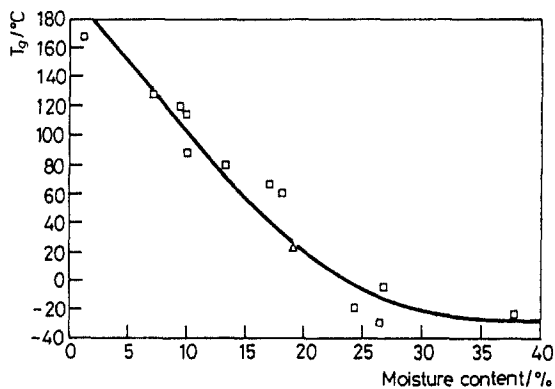


Fig. 7 Effect of moisture content on T_g of starch. W_g identified by dielectric spectroscopy is indicated (Δ)

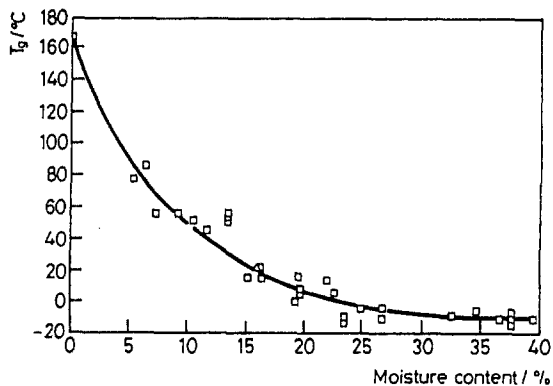


Fig. 8 Effect of moisture content on T_g of bread. W_g identified by dielectric spectroscopy is indicated (Δ)

Comparison between dielectric and TMA measurements

DS and TMA identified about the same W_{gs} , the moisture contents at which T_{gs} were equal to 22°C, for bread and starch samples, whereas for gluten, DS gave a slightly higher W_g value, as described and explained earlier.

Conclusions

Both DS and modified TMA are useful methods for T_g determination of gluten, starch, and bread. Microwave-frequency DS has the potential for determining T_g curves, if automatic temperature scanning could be achieved. The difference in the W_g values for gluten at 22°C determined by TMA and DS might be due to a difference in the relaxation time scales for rheological and dielectric properties of such materials.

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