Journal of Thermal Analysis, Vol. 47 (1996) 1315-1328

USE OF DYNAMIC MECHANICAL THERMAL ANALYSIS (DMTA)
Glass transitions of a cracker and its dough

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Abstract

A Mark III DMTA (Polymer Laboratories, Loughborough, U.K.) was used to measure the glass transition temperatures (T_g) of a commercial cracker and its dough, each equilibrated to various water activities covering a range of 0.11–0.75 for the cracker and 0.11–0.90 for the cracker dough. DMTA measures the change in the elastic modulus (E') and loss modulus (E''), as well as that in tanδ (E''/E'), with temperature. The change in the elastic modulus with temperature for the two systems followed a pattern similar to that found for complex food polymers (gluten, amylopectin), with T_g decreasing as moisture content increased. Baking did not change the location of the glass transition curve (T_g *vs.* moisture content); i.e. the curves for raw dough and baked finished product were somewhat superimposable, and similar to the published gluten curve, indicating that for this type of cracker containing ~5% sugars, the protein fraction is most responsible for the T_g curve.

Keywords: cracker T_g, DMTA, glass transition, gluten

Introduction

As first emphasized by the pioneering work of Levine and Slade [1], baked, extruded and dehydrated foods can be treated as biopolymeric systems that can exist in either a glassy or rubbery amorphous state and can undergo a glass transition with a change in temperature and/or moisture content. This polymer science–glass transition approach can provide a clear understanding of the texture of either crisp or soft cereal-based snacks as a function of composition, temperature and moisture content [2]. There are a number of techniques available to the food scientist for measuring the glass transition temperature (T_g) of food materials [2–4]. The glass transition is accompanied by a change in various physicochemical properties, including volume expansion, heat capacity, mechanical modulus, rotational mobility of diffusing molecules, and proton mobility of water [2, 3]. Unlike synthetic polymers, foods are characterized by inhomogeneity and complexity, and the measurement of T_g is not an easy task.

0368–4466/96/ $ 5.00

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In many cases, the choice of technique depends exclusively on the availability of equipment.

Differential scanning calorimetry (DSC) has been the most widely used technique, and is a method appropriate for measuring the T_g, as well as the temperatures of denaturation of proteins and crystallization reactions [5]. The glass transition region is indicated by a diffuse, step-like transition in heat capacity, and either the initial temperature, midpoint or endpoint of the transition has been defined as T_g [3, 4]. A glass transition measured by DSC for gluten, the major complex protein fraction of wheat flour, was first reported by Slade in 1984 [2]. Hoseney *et al.* [6] also used DSC to determine the glass transition curve of gluten, and concluded that gluten is a biopolymer plasticized by water, such that its T_g decreases with increasing water content. The effect of water content (in the range of 4–14% (wb)) on the glass transition of glutenin, a subfraction of gluten, was studied by Cocero and Kokini [7], using both DSC and mechanical spectroscopy at a heating rate of 5°C min^{-1}. The T_g dropped from 132° at 4% moisture to 28°C at 14% moisture, or 11° per % moisture. Based on this, they suggested that small deviations in the moisture content or temperature of a baked product could result in major changes in the rheological properties of the finished product, and consequently in the texture perceived by the consumer. DSC curves were generally in agreement with mechanical spectrometry scans. Their DSC results agreed well with the water-content dependence of the glass transition for wheat gluten, reported by Hoseney *et al.* [6]. The effect of water content on the T_g of the other major wheat-protein fraction, gliadin, was evaluated by de Graaf *et al.* [8], using mechanical spectrometry and DSC in the moisture ranges of 6.2–27.2% and 0–16.6%, respectively. Their DSC results were in agreement with those obtained by Cocero and Kokini [7] and Hoseney *et al.* [6]. The glass transition curve as a function of moisture for gliadin fell below those for glutenin and gluten, at moisture contents below 8%. It was suggested [8] that this difference might be due to the higher molecular weight of glutenin, and to the higher concentration of hydrophilic amino acids on the gliadin chain, which might enhance its plasticization. Overall, it appears that the effect of water content on T_g of glutenin and gluten is similar, suggesting that glutenin is largely responsible for the mechanical properties of gluten [7]. Cocero and Kokini [7] and Kokini *et al.* [9] attributed the higher glass transition curve of glutenin, compared to gliadin, to the disulfide crosslinks present in glutenin, and concluded, as did de Graaf *et al.* [8], that glutenin is the component that determines the glass transition behavior of the gluten network.

Le Meste *et al.* [10] used a modified thermal mechanical analysis (TMA) method to study the glass transition of white pan bread, a true composite, processed food. TMA measures T_g by detecting changes in thermal expansion coefficient. In their study, they combined TMA with an oscillating load and were thus able to monitor both mechanical and volume changes (expansion) [10]. TMA, by itself, cannot be fully reliable, because volume changes may be related to gas bubble expansion in bread; however, it was concluded that mechanical softening is a more satisfactory indicator of the glass transition than are volume changes [10].

Nuclear magnetic resonance (NMR) of water protons was used by Kalichevsky *et al.* [11] in a study of the glass transition of amylopectin from waxy maize starch. The decay time for the mobility of water in amorphous amylopectin was obtained after the application of a 90° magnetic pulse. The decay corresponds to two components, one from rigid and one from mobile protons. On passing through the glass transition, the decay time corresponding to the rigid component begins to increase with increasing temperature; this is attributed to the onset of an increase in frequency of the motions of groups containing hydrogen. Kalichevsky *et al.* [11] also used an Instrón texturometer to measure Young's static, elastic modulus by a three-point bend test; the modulus was calculated from the initial slope of a force *vs.* deformation plot.

Dynamic mechanical thermal analysis (DMTA) is a major method used by the synthetic polymer industry to determine the T_g of films [4]. T_g is measured as the point of initial decrease or the midpoint of the change in elastic modulus (E'), the point of initial increase or the midpoint of the change in loss modulus (E''), as well as the loss peak in $\tan\delta$ (E''/E'), as a function of temperature. DMTA is suited to the study of texture, since changes in modulus define changes in the texture of foods, as related to changes in physical properties between the glassy solid and rubbery liquid states [2, 3]. The drop in modulus observed at T_g is on the order of 100–1000 fold, which makes T_g much easier to measure by DMTA than by DSC, where the change in specific heat at T_g can be very small [3, 4]. At constant temperature, a frequency scan (dynamic mechanical oscillation) can be performed to measure E' and E''. In addition, using constant frequency, a scan of modulus *vs.* temperature can be performed. A large decrease in E' and a peak in E'' are observed in the temperature range in which the main chain had been frozen in the glassy state. A limitation of the method is the potential drying out of the sample as temperature increases. To avoid this, the samples are scanned rapidly, although this also introduces another error, in that the sample temperature may lag.

In one of the first studies using DMTA to analyze glass transitions in foods, Wetton and Marsh [12] tested a series of products, including cheese, casein, gluten, soy isolates, starches and chocolate. They demonstrated the great potential of this technique for applications to materials other than synthetic polymers, and especially in food systems, including composite processed products such as cheese and chocolate. Subsequently, Kalichevsky *et al.* [13] used DMTA (Polymer Labs Mark I) to measure T_g for wheat gluten over a moisture range of 10–22%. T_g was evaluated from the initial drop in E' and from the peak in tanδ (using a heating rate of either 2 or 5°C min^{-1}), as well as from the transition midpoint measured by DSC (Perkin-Elmer DSC-2, heating rate of 10°C min^{-1}. In that study, humectants were also added in a ratio of 1:10 humectant:gluten; added sucrose decreased gluten's T_g by 5°C, fructose by 7°C, and glycerol by 10°C. Added glucose did not affect T_g of the mixture at a 1:10 ratio, but decreased T_g by 4°C when added at a 1:5 ratio.

When comparing the T_gs measured for foods by different techniques, one immediately recognizes that T_g is not a unique temperature, but depends on the criteria used for its determination. As noted above, mechanical methods, and DMTA in particular, are more sensitive to the glass transition than is DSC, and mechanical properties are better correlated with changes in texture of food systems that interest the food scientist. Kalichevsky *et al.* [11] compared DSC, DMTA, Instron texturometer, and NMR in determining the T_g of amylopectin. Their DSC midpoint values fell between the E' midpoint temperatures and tanδ peak temperatures, but closer to the E' values. They were not able to detect secondary, low temperature transitions with DSC, whereas DMTA revealed such transitions. It was this capability of DMTA that assisted in their investigations of the effect of degree of crystallinity on T_g of amylopectin and of phase separation in mixtures of gluten and sugars. However, both DSC and DMTA became more difficult to perform with increasing sample crystallinity. NMR produced T_g values even lower than those from DMTA. This was indicative of the fact that NMR is sensitive to different degrees of molecular mobility and structure [11]. Kalichevsky *et al.* [13] also compared DMTA and Instron-texturometer results for gluten. The modulus values from the two methods were in general agreement, but the DMTA values were slightly lower than the ones obtained with the Instron. This small difference was attributed to the different strain rates for the two techniques and to errors in measuring sample dimensions for DMTA measurements. In any case, all of the methods described above can be used to produce a state diagram (T_g *vs.* moisture content), which can be valuable to the food scientist in evaluating textural changes in foods during processing and storage [2, 3, 9], and can explain the reasons for changes in crispness as a function of water activity, as found previously by Katz and Labuza [14]. The objective of this work was to show that DMTA is an appropriate method for measuring the T_g of processed, cereal-based food products, such as a cracker and its dough prior to baking.

Materials and methods

Cracker

A commercial cracker was provided by the manufacturer (GBB, Herentals, Belgium). This cracker was received in 100 g (3.5 oz) packages containing 22 pieces.

Dough

The corresponding cracker dough was prepared according to the standard recipe provided by GBB. All ingredients were provided by the cracker manufacturer, with the exception of water and fresh whole egg. The ingredients were mixed in the mixing bowl of a Brabender farinograph (C. W. Brabender Instruments, South Hackensack, NJ). The dough was removed from the mixing bowl and immediately stored (for no more than one hour) in sealed glass jars, prior to further handling. The basic formula used was one for a low moisture dough (~20% on total weight basis) with ~5% (db) added sugars and a chemical leavening agent. Specifics of the cracker-dough formula are proprietary to GBB.

Sample preparation

The obtained mass of dough was shaped into rectangular pieces with dimensions of 13 mm width, 10 mm thickness, and length that varied between 2.5 and 3.0 cm. These sample dimensions were previously determined to result in DMTA measurements with maximized signal-to-noise ratio. The length of the dough piece was variable, because the sample length was determined by the choice of clamping frame on the DMTA head. Prior to each DMTA run, crackers were removed from their desiccators, and a piece was cut into a rectangular shape with dimensions of 10 mm width, 5 mm thickness and approximately 2 cm length (5 mm overall length).

The shaped dough pieces, or whole crackers before cutting, were placed in triplicate in a series of desiccators containing saturated salt solutions. The number of whole crackers in each desiccator was sufficient to give several samples of the dimensions required for DMTA runs and triplicate samples for final moisture-content determination. Similarly, three additional dough pieces were placed in each desiccator for final moisture-content determination. The water-activity ranges used were 0.11 to 0.75 for the cracker and 0.11 to 0.90 for the dough. The desiccators were kept at room temperature (approximately 23 °C).

The dough pieces and crackers were equilibrated in desiccators for at least three weeks, to reach their equilibrium water contents. The Greenspan values [15] for the saturated salt solutions at room temperature were taken as the water activities of the equilibrated samples. The solutions used were LiCl (a_W 0.11), $MgCl_2$ (0.33), KCO_3 (0.43), $Mg(NO_3)_2$ (0.53), $NaNO_2$ (0.64), NaCl (0.75), KCl (0.84), and $BaCl_2$ (0.90).

Moisture content and moisture sorption isotherm determination

The equilibrium water contents of the cracker and dough at each water activity were determined by air-drying at 130°C for 30 min. The average values of equilibrium water content (g water/g solids) were plotted *vs.* water activity to

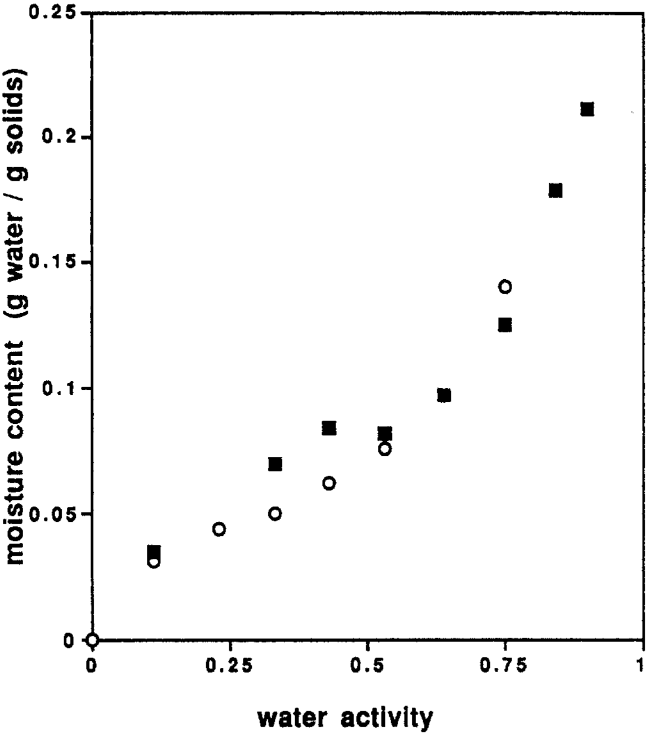

Fig. 1 Comparison of the moisture adsorption isotherms (g water g^{-1} solids *vs.* water activity) at 23°C for the initial dough (■) and the finished cracker (o)

construct working isotherms, using the ISOTHERM/BET/GAB computer program [16]. Figure 1 shows the working isotherms for the cracker and dough.

DMTA

T_g measurements were performed using a Mark III DMTA from Polymer Laboratories (Loughborough, U.K.). The PL-DMTA Mk III operates at constant displacement amplitude, resulting in a constant strain amplitude for a given sample geometry. This constant amplitude is maintained throughout an experiment. The magnitude of the displacement can be chosen from 10 possible settings (strain range –1 to 8). This strain range corresponds to an amplitude range of 5 to 128 μm. For this research, a strain setting of 2, corresponding to a 16 μm amplitude at a frequency of 1 Hz (1 cycle/s), was chosen based on consultation with the instrument manufacturer. The mode of deformation chosen was single cantilever clamped-bending, which is best suited for materials such as crackers, which have low to medium moduli (10^6 to 10^9 Pa), according to the instrument manufacturer. The small frame and flat-face clamps were clamped manually, to a point where samples were secured without braking, because of the fragility of the samples. Heating rates of 3°C and 10°C min^{-1} were used. T_g was reported as the temperature where the slope in E' changed sharply, i.e. the onset temperature, and was determined from the intercept of the extrapolated line of the initial modulus and that of the steepest slope, and from the point where the loss tangent just began to ascend. It should be noted that throughout the remaining text, the T_gs referred to are onset values.

Results and discussion

Figure 2 shows a typical DMTA plot for the dough at a moisture content of 7% (db). In all such plots, the elastic modulus showed a sharp drop on the order of about 100-fold. According to Sperling [4], the elastic or storage modulus in the glassy state is approximately 100 to 1000 times higher than the corresponding modulus in the rubbery state for synthetic polymers. The tanδ curve exhibited a main peak, characteristic of a glass transition, as well as one or more smaller peaks at temperatures lower than that of the glass transition (e.g. in Fig. 2, one occurs at ~17°C). Such smaller peaks have been attributed to local motions of side-chain groups on a polymer, while the main peak has been attributed to motions of the polymer backbone, associated with the major glass transition [3, 4, 11]. Wetton and Marsh [12] and Kalichevsky *et al.* [11] observed similar small transitions at temperatures lower than those associated with the glass transitions of cheese and amorphous amylopectin, respectively. Wetton and Marsh [12] attributed these smaller peaks for cheese to fat melting and the main peak to mobilization of the protein matrix. Kalichevsky *et al.* [11] attributed the low temperature peaks in the tanδ curve for amylopectin to the onset of short-range motions, and the main transition to the onset of backbone-chain motions. It can be noted in Fig. 2 that as soon as the T_g in E' was exceeded, the tanδ curve became quite irregular, with several additional peaks. This irregularity could be attributable to inhomogeneity of the samples at the molecular level and to moisture loss at temperatures above 60°C.

Figure 3 shows the glass transition curve for the cracker, as measured from E' analysis by DMTA at a heating rate of 3°C min^{-1}. As can be seen, the cracker is a water-plasticizable material, with a T_g that decreases with increasing water content. Its T_g values (Table 1) ranged from approximately 155°C to approximately –6°C in the moisture range from 0.03 to 0.14 g water/g solids (2.9 to 12.3 % wb), i.e. a drop of about 15°C per 1% water (wb), which is typical of many food polymers [2, 12, 13]. Based on the working isotherm and glass transition curve of the cracker, the critical water activity at which the cracker entered the rubbery state at room temperature was about 0.65, for a moisture content of 10.7% (wb). Previous sensory analysis of a saltine-type cracker by Katz and Labuza [14] showed a critical water activity for loss of crispness at around 0.4, for a moisture content of 6.5% (wb). Georget *et al.*

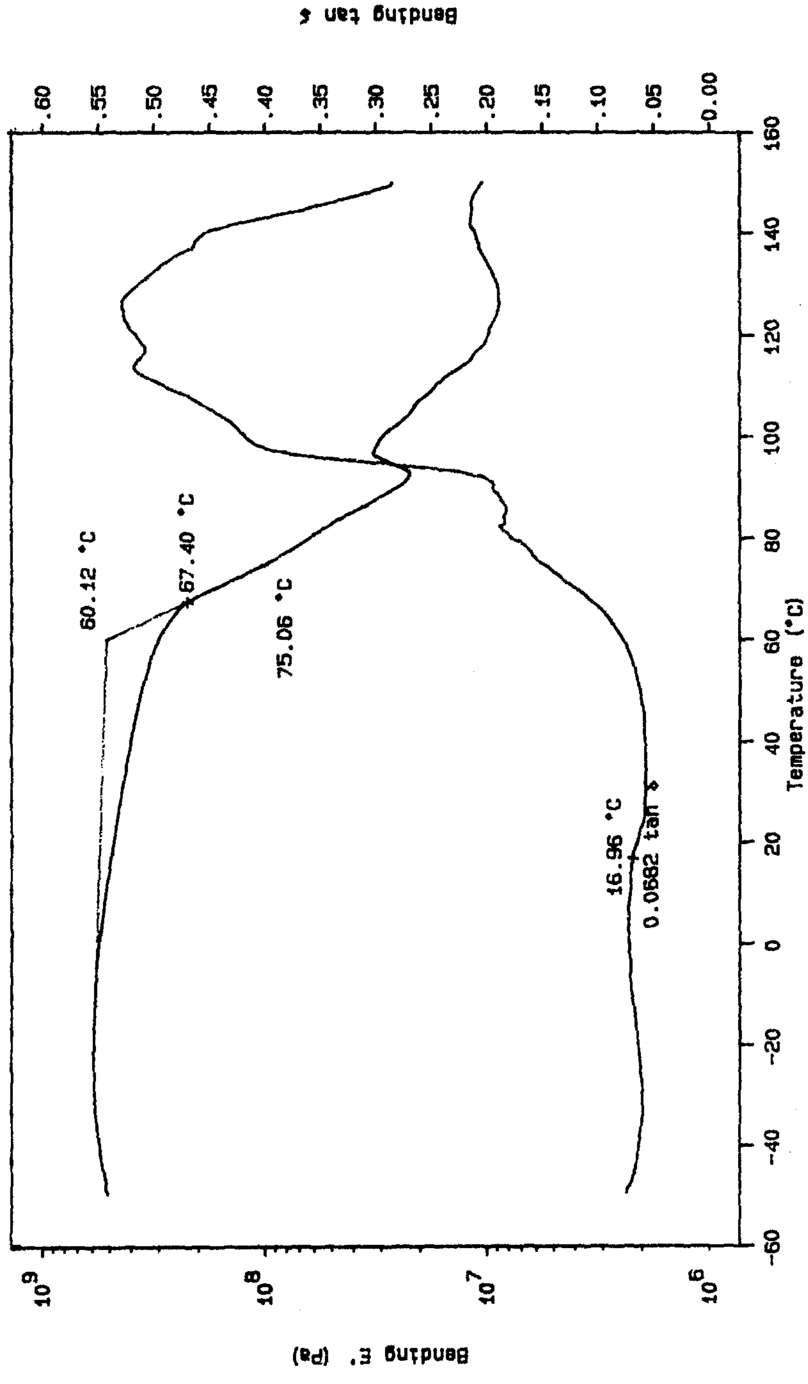

Fig. 2 DMTA plot for cracker dough with a moisture content of 7% (db), heated at 3°C min^{-1}

Table 1 Glass transition temperatures of cracker and dough, as measured by DMTA

a_w	Cracker			Dough		
	Moisture	T_g/°C,	T_g/°C,	T_g/°C,	Moisture	T_g/°C,
		tanδ analysis	E' analysis	E' analysis		E' analysis
	g_{water} /g_{solids}^{-1}	3°C min^{-1} (avg.±sd)	3°C min^{-1} (avg.±sd)	10°C min^{-1} (avg.±sd)	g_{water} g_{solids}^{-1}	3°C min^{-1} (avg.±sd)
0.11	0.0314	138±7	155±15	72±3	0.035	60±3
0.23	0.0442	63±12	57±3	72±3		
0.33	0.0499	57±6	59±6	67±2	0.070	55±2
0.43	0.0621	46±10	55±1	65±3	0.084	50
0.53	0.0760	35±4	45±6	63±3	0.082	52±2
0.64	0.0975	25±2	23±8	23±4	0.097	40±2
0.75	0.1400	–6±1	12±1	16±11	0.125	13±3
0.84					0.179	–9±1
0.90					0.211	–9±1

[17] found that Young's modulus for low-moisture slabs of gluten showed a significant drop at about 10% moisture (a_W not reported), and Peleg [18], analyzing the data of Sauvageot and Blond [19] for sugar-containing, ready-to-eat cereals, reported a drop in sensory score for crispness at a water activity of about 0.5 (moisture not reported). The differences in these similar results probably arise from differences in sample compositions.

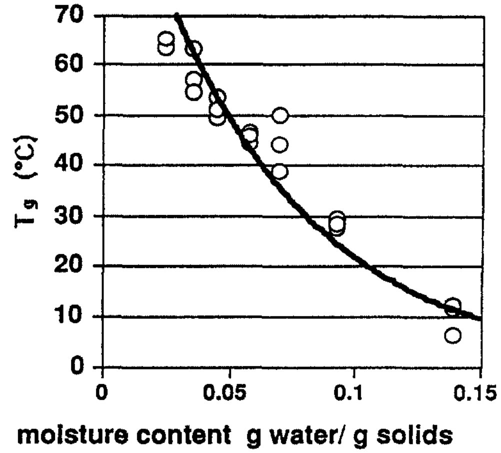

Fig. 3 Glass transition curve (T_g vs. moisture content) for a commercial cracker, determined from E' analysis by DMTA at a heating rate of 3°C min^{-1}

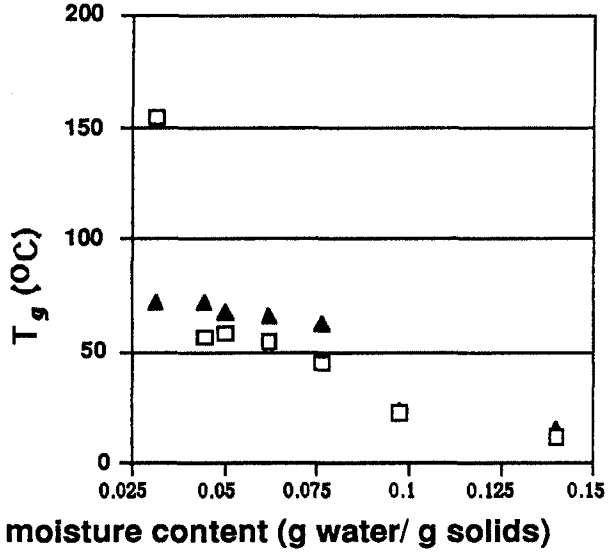

Fig. 4 Comparison of the glass transition curves for the cracker, analyzed by DMTA at 3°C min^{-1} (□) and 10°C min^{-1} (▲)

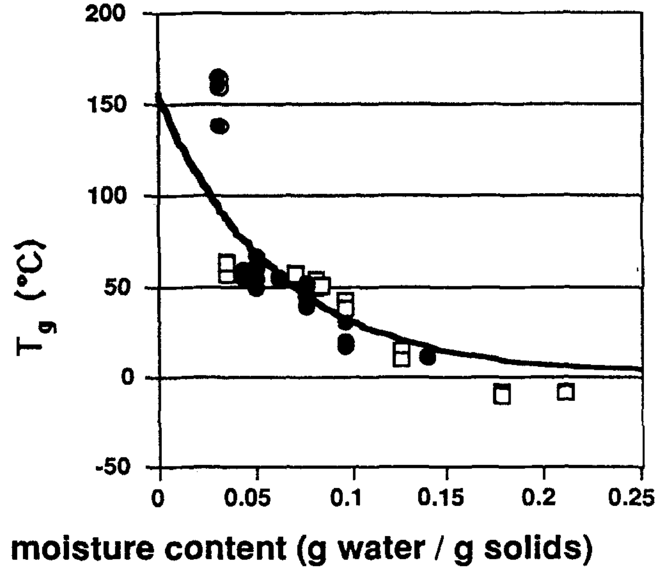

Fig. 5 Comparison of the glass transition curves for the cracker (■) and its dough (□)

Figure 4 compares the glass transition curves for the cracker, determined by DMTA at two different heating rates (3 and 10°C min^{-1}). As can be seen from this Figure and Table 1, the higher heating rate resulted in a higher glass transition curve for the whole moisture range examined. Kalichevsky *et al.* [11] compared two heating rates, 2 and 5°C min^{-1}, in their DMTA study of the glass transition in amylopectin, and stated that no difference was found in the T_g values measured at the two heating rates, but no results were given to support this statement. It is possible that the two rates they tested were too similar to reveal significant differences. However, Chuy and Labuza [20], in a study of the glass transition in four powdered infant formulas, found a significant increase (5 to 10°C) in T_g with increasing heating rate.

Figure 5 compares the glass transition curves for the cracker and its dough. In this case, all replicates of the E' measurements were plotted to show the range in the T_g measurement. As can be seen (Table 1), the two materials had very similar glass transition curves, except at the lowest water content, where the T_g value for the dough was much lower than that for the cracker. This might be attributable to the fact that the detection of T_g for the cracker at that water content was difficult because of the cracker's fragility; this was not the case for the dough. Figure 5 shows that the baking process did not appear to have a major effect on the glass transition curve for the cracker dough, compared to that for the baked finished product. In other words, it appears that baking did not change the dough ingredients or ingredient interactions responsible for the mechanical behavior of the dough, possibly supporting the suggestion that amylose and amylopectin are not primarily responsible for the observed glass/rubber transition. Svensson and Eliasson [21] recently showed that greater than 20% water content is necessary to allow crystallization/gelatinization changes in wheat starch. From Fig. 5, it appears that water contents of 0.05 g water/g solids or higher had less of an effect on T_g of the dough, since the glass transition curve shows a more shallow downward slope at these water contents. Since the actual degree of gelatinization of the starch was not measured, it can only be speculated that this does not contribute to T_g.

In order to put the glass transition curve for the cracker in perspective, compared to similar data for other bakery products and ingredients, the T_g results for various components and products, discussed previously by other workers [7, 8, 10, 11, 13], were examined in Fig. 6. The glass transition curve for the cracker includes error bars for the T_g measurement. It is evident from Fig. 6 that the cracker had the lowest glass transition curve, compared to those for various major cereal ingredients and commercial white bread. Gluten, a major, complex polymer in wheat flour, has a T_g curve closest to that of the cracker, which might be expected, if starch were not gelatinized during baking of the cracker, as speculated above. As noted earlier, the glutenin curve almost superimposes on the gluten curve. Glutenin has recently been under intense investigation as the key component in the elastic behavior of baked goods, owing to its sulfide linkages [22]. Bread, another cereal-based product, also has a glass

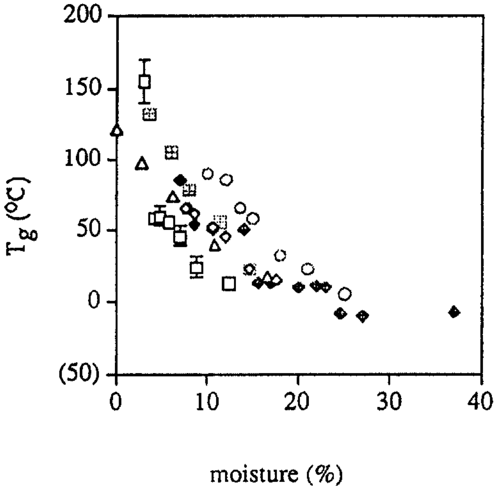

Fig. 6 Comparison of literature data for glass transition curves for cereal ingredients and whole cereal products with the glass transition curve for the cracker; (□) cracker this study, (◊) gluten by E' [13], (o) amylopectin by E' [11], (Δ) gliaden by DMS [8], (⊞) glutenin by DMS [7], (◆) read by TMA [10]

transition curve that superimposes on the gluten/glutenin curves. As noted earlier, the lower position of the curve in Fig. 6 for the cracker could be due to the presence of sugars in the cracker [13]. Recently, Georget *et al.* [23] showed the effect of added sugar in lowering the T_g curve of flaked wheat cereals. That this subject is complex is supported by an overview of snack foods [24], in which it was reported that with increasing dextrose equivalent (DE) of maize maltodextrins (from ~6 to 21), there was an increase in sensory crispness perception for extruded corn-based snacks, exactly opposite to expectations based on previously published relationships between T_g and DE [25]. Unfortunately there was no information on moisture content or the type of sensory analysis used by de Cock [24]. Thus, establishing the T_g curve for any finished, fabricated food product, in relation to the T_g for each of its ingredients, and relating T_g to sensory properties will continue to be of great value in understanding foods at the material science/polymer science level.

Conclusions

Knowledge of the physical state and state diagram of food materials (ingredients), although useful, does not necessarily take into account the effect of ingredient interactions on the mechanical behavior of a finished product. Techniques other than DSC can and have been used to measure the T_g of food materials. However, very few studies have attempted to apply those techniques to finished, processed products. The present work suggests that DMTA is a useful method for measuring the T_g of finished bakery products such as crackers and their doughs. Of much interest is the finding that the glass transition curves for the cracker and its dough were very similar. This suggests that baking did not change the ingredients or ingredient interactions responsible for the mechanical behavior of the cracker dough. Based on comparisons with state diagrams for various food polymers, it was shown that crackers are plasticized by water [2], resulting in T_g values that decrease with increasing water content. Gluten or its glutenin fraction may be the most important component in determining the mechanical behavior of such products. Undoubtedly, such a hypothesis may not take into consideration possible ingredient interactions, and more research is needed in this area.

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We wish to acknowledge GBB, Herentals Belgium, for support in the purchase of the DMTA and for providing the crackers and dough. This study was supported in part by a grant (#18-72) from the University of Minnesota Agricultural Experiment Station and is presented as paper # 22169.

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