Journal of Thermal Analysis, Vol. 47 (1996) 1329-1338

USE OF A THERMOMECHANICAL ANALYZER
Study of an apparent glass transition in cookie dough*

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Abstract

The ThermoMechanical Analyzer (TMA) is a sensitive instrument that measures dimensional changes such as those occurring during glass transitions. Knowledge of the glass transition temperature (T_g) may provide a better understanding of many food systems. Cookie dough is a food system that appears to be affected greatly by an apparent glass transition of the flour protein. Hard-wheat-flour cookie doughs underwent an apparent glass transition at a lower temperature (71°C) than did soft-wheat-flour cookie doughs (78°C). Decreasing the sugar level in the dough decreased both the set time and the apparent T_g. Set time and apparent T_g were highly correlated ($r=0.971$ soft; $r=0.989$ hard).

Keywords: cookie dough, glass transition, TMA

Introduction

The glass transition temperature (T_g) is one of the most important properties of a polymer and can affect many of its physical properties [1]. Although the T_g of many individual food components and model systems has been investigated (Z), relatively little is known about the T_g of actual cereal-product systems.

The differential scanning calorimeter (DSC) is currently the most popular instrument used to measure thermal behavior in food systems (Z). The T_g is seen in the DSC as a step change in heat capacity. However, measuring T_g with the DSC is difficult because of its limited sensitivity. The concentration of the polymer of interest in a food system can be relatively dilute; therefore, a large sample size is required. Interpretation of the results also can be difficult.

The most convenient way to measure T_g is to measure the volumetric properties of the polymer [1]. In the glassy state, molecular motion is restricted to vibrational and rotational motion. The transformation from glass to rubber in-

* Contribution No. 95-512-J, from the Kansas Agricultural Experiment Station.

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0368-4466/96/ $ 5.00

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creases chain mobility and causes a dimensional change. The thermomechanical analyzer (TMA) is a sensitive instrument that can measure the small dimensional changes occurring in polymers. The TMA offers greater sensitivity than does the DSC for detection of lower intensity transitions such as the glass transition [2]. The TMA has been used for many years in the plastics industry and to characterize mechanical properties of polymer systems [3–5]. However, its use in the food industry [3–5] has not been established yet.

Sugar-snap cookies spread in the oven during baking, while some other cookies (e.g., sheeted rotary-cut cookies such as animal crackers or Vienna fingers) do not. The major differences between these two types of cookies are the higher level of sugar in the sugar-snap formula (60 *vs.* 20%, based on flour weight) and the formation of a gluten web in the non-spreading cookies.

Time-lapse photographs taken during baking of sugar-snap cookies show that the cookie diameter expands essentially linearly until a certain time, and then it suddenly stops expanding [6]. The point at which it stops has been defined as the set time. It has been suggested that the cookie set time is the time at which a continuous gluten web is formed [7].

An explanation given for this phenomenon is that the gluten is not developed into a web during mixing; thus, the continuous phase in the sugar-snap cookie dough is a sugar syrup. Therefore, the flour particles in the dough remain intact and discontinuous. It has been suggested [7] that during baking, the gluten goes through an apparent glass transition, thereby gaining mobility that allows it to interact and form a web. The viscosity of the continuous gluten web is sufficient to stop the flow or expansion of the cookie dough.

It is well known that soft wheat flour produces thin, tender, large cookies, whereas hard wheat flour produces thick, hard, small cookies. Abboud *et al.* [6] showed that cookies made with soft wheat flour spread at a faster rate and for a longer time before setting than did cookies made with hard wheat flour. Yamazaki [8] showed that cookie doughs made with good cookie flour started to increase in viscosity at a higher temperature than did cookie doughs made with poor cookie flour. Abboud *et al.* [6] concluded that a temperature-mediated change in viscosity was responsible for the setting of cookie diameter.

Doescher *et al.* [7] reported that the T_g of flour correlated highly with the set time of cookies. Low sensitivity, small sample size, and the occurrence of other thermal events, such as fat melting and sugar dissolving, which obscured the T_g of the gluten, did not allow Doescher *et al.* (7) to test actual cookie doughs in the DSC. They were forced to extrapolate measurements made on flour to the changes occurring in the cookie dough. The TMA has a higher sensitivity, uses a larger sample size, and measures only events that change the volume of the sample. These advantages allow it to be used to test actual food systems such as cookie dough.

The objectives of this study were to: 1) show that the TMA can be used to effectively study food systems such as cookie dough, and 2) confirm that the set time of cookie dough is caused by an apparent glass transition of the gluten protein in the flour.

Materials and methods

Cookie ingredients

A commercially milled, untreated, soft white winter wheat flour containing 12.3% moisture, 0.43% ash, and 7.65% protein (14% moisture basis) was obtained from Mennel Milling Company (Fostoria, OH). A commercially milled, untreated, hard red winter wheat flour containing 12.7% moisture, 0.50% ash, and 10.8% protein (14% mb) was obtained from Cargill (Wichita, KS). Superfine sucrose was obtained from C&H (Concord, CA). Nonfat dried milk was supplied by American Ingredients (Kansas City, KS). Crisco, a commercial, hydrogenated, all-vegetable shortening manufactured by Procter and Gamble, was used. Sodium bicarbonate, sodium chloride, and ammonium chloride were reagent grade.

Cookie baking

Cookie doughs were prepared using AACC Method 10–52 [9]. Water absorption was 25% (flour weight basis, fwb) for all formulations, unless otherwise specified. Sucrose levels were 60% (control), 50%, 40%, or 30% (fwb). The cookies were baked in a reel oven (National Manufacturing Co. Lincoln NE) at 205°C for 10 min. Cookie diameter was measured after the cookies had cooled completely. The average of three different measurements per two cookies is reported. A minimum of two trials was baked for each treatment.

Flour preparation for TMA

Soft and hard wheat flours were stored for one week in a desiccator containing saturated sodium acetate, to adjust the flour moisture content to 13%. Twenty g aliquots of the flours were formed into pellets using a Carver hydraulic press set at a pressure of 3000 psi. Each pellet had a diameter of 13 mm and a thickness of 2 mm. The pellets were stored in the desiccator for one week to regain moisture lost during pellet preparation. A minimum of two pellets was tested for each flour.

Cookie dough preparation for TMA

Cookie doughs were prepared using AACC Method 10–52 [9] with two modifications: chemical leavening agents were omitted and sodium chloride level was increased to 0.4 per dough (dough from 40 g of flour). In prelimi-

nary trials, expansion of the cookie dough by the leavening agents made it impossible to measure the T_g [10]. The sodium chloride level was increased to compensate for salt ordinarily produced in the chemical leavening reaction.

TMA method

A ThermoMechanical Analyzer (TMA) (Rheometric Scientific, Piscataway, NJ) was used to determine the apparent T_g of the flours and cookie doughs. This instrument measures the change in dimension of a sample as a function of temperature. The dimensional change causes displacement of a counter-balanced probe touching the top surface of the sample. The displacement of the probe induces a voltage change in a linear variable-displacement transducer (LVDT). This change in voltage is then converted to a measure of the change in dimension of the sample. The instrument has a sensitivity of 0.001 mm.

A sample of cookie dough approximately 2 mm thick was placed in the TMA, and a microscope cover glass was placed on top of the dough. The cover glass prevented direct contact between the dough and the TMA probe and eliminated penetration by the probe through the dough as the dough softened during testing. The samples were heated from 25 to 100 °C at a rate of 1 °C min^{-1}.

Time-lapse photographs

Photographs of the cookies were taken, at 30 s intervals during baking, with a camera mounted to the oven door. Guidelines were drawn 8.9 cm from one end of a baking sheet (parallel to edge) and down the center to form a cross. Cookie dough was placed on the sheet, rolled, and cut so that the cookie was centered over the cross, to assure that the cut cookie was in the same position in every trial. A small metal bar of known dimension was placed at a marked position on the guideline beside the cookie, so the actual diameter of the cookie could be determined from the photographs. The baking sheet was placed on a stationary shelf in the oven. The shelf was adjusted so that the camera was at the same level as the cookie. Cookie diameter was measured directly from the photographs and adjusted to scale. Cookie set time was taken as the time at which the cookie stopped increasing in diameter. A minimum of two trials was baked for each treatment.

Lubricated uniaxial compression

The lubricated uniaxial compression method described by Bagley and Christianson [11] was used to measure the biaxial, elongational viscosity of cookie doughs made with soft wheat flour. Cookie doughs were prepared according to AACC Method 10–52 [9], with the exception that the cream, water, and leavening solutions were mixed for 10 min before the flour was added. Cookie

doughs were either tested immediately or after being heated to 80°C in an electrical-resistance oven [6] and then cooled to 30°C. For testing, cookie dough was deposited in four separate pieces onto a well-greased cookie sheet and rolled to a thickness of 7 mm. A single, 40-mm-diameter disk was cut from each rolled dough piece. The dough pieces were coated generously with mineral oil to lubricate the dough and prevent adhesion to the probe during testing. The dough pieces were compressed with a teflon-coated, 50-mm-diameter probe attached to a TA.XT2 Texture Analyzer (Texture Technologies, Scarsdale, NY/Stable Micro Systems, Godalming, UK). The cookie doughs were deformed to 50% strain at a speed of 0.4 mm sec^{-1} and held for 20 s. The elongational viscosity was calculated with the following equation:

$$\text{Elongational Viscosity} = 2Fh/R^2 V_z$$

where F is the total force required to deform the dough, h is the dough height after compression, R is the radius of the sample after compression, and V_z is the cross-arm speed.

Data analysis

Data were evaluated by analysis of variance and least significant difference, using the Statistical Analysis System (SAS Institute, Inc., Cary, NC).

Results and discussion

Optimization of TMA procedure

A few operating parameters had to be modified when using the TMA for testing food-polymer samples [10]. Preliminary trials using the manufacturer's suggested heating rate of 10°C min^{-1} showed this heating rate to be inappropriate for food-polymer samples. The polymers in food systems are typically more dilute than are the polymer systems tested by other industries. Consequently, the suggested heating rate was too fast and reduced the sensitivity of the test, giving inconsistent results. A heating rate of 1°C min^{-1} gave reproducible results.

In the TMA procedure, liquid nitrogen can be used to lower the starting temperature of the sample. The manufacturer suggests that after cooling, the supply of liquid nitrogen should be continued throughout the experiment. This procedure was found to be inappropriate for the food samples studied in this work. The liquid nitrogen dried the sample, causing it to shrink and producing a dimension change. Therefore, liquid nitrogen was not used.

TMA of cookie dough

Gluten is known to be a glassy polymer at room temperature when it is dry (Z), but it goes through a glass transition when wetted to about 16% moisture

[12]. In a cookie dough, as described above, the aqueous phase is a sucrose syrup. Sucrose can act as a plasticizer, but it is much less effective than water, because of its larger molecular weight [1, 2, 13]. Thus, with the limited water in cookie doughs (25% based on flour), we might expect the gluten T_g to be considerably above room temperature.

Figure 1 shows the changes that occur during heating of a soft-wheat-flour cookie dough in the TMA. At about 40°C, the dough begins to soften (height decreases) as the shortening melts and crystalline sugar dissolves [14]. At various temperatures, depending on the sugar concentration, the dough begins to expand. Chemical leaveners were not added to the formula, so the expansion was not caused by leavening reactions. The expansion was also not caused by the hydration of the flour particles, because a heat-of-hydration exotherm was not seen in the DSC [7].

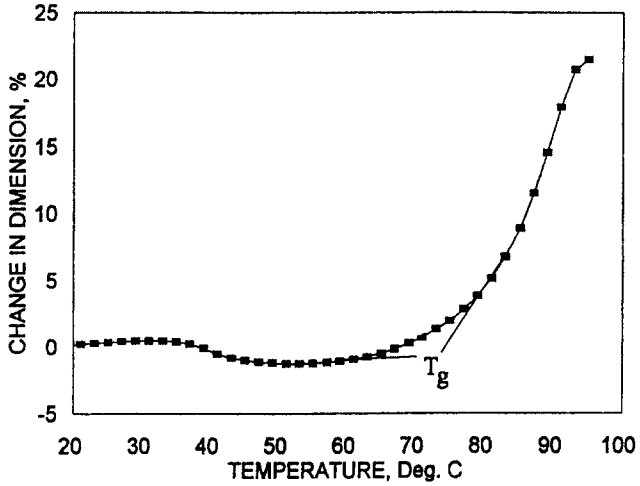

Fig. 1 TMA curve for cookie dough made with soft wheat flour and 45% sugar (fwb). Dough softening caused by melting of shortening and sugar, occurred at about 40°C, and dough expansion occurred as gluten went through an apparent glass transition at about 73°C

Below the transition point in the TMA curve, the cookie dough is a viscous mass that can expand if the rate of gas production is sufficient. For the dough to expand, the rate of gas production must be greater than the rate of gas diffusion to the surface of the cookie dough. Thus, the dough expands, when leavening agents react to produce gas at a rapid rate (Fig. 2). Cookie doughs made without leavening agents soften rather than expand.

Above the transition point, the expansion is an order-of-magnitude larger than would be expected from a glass transition. This large expansion probably occurs because the dough is expanded by water vapor. However, if the expansion were caused only by water vapor, the volume of the cookie dough should

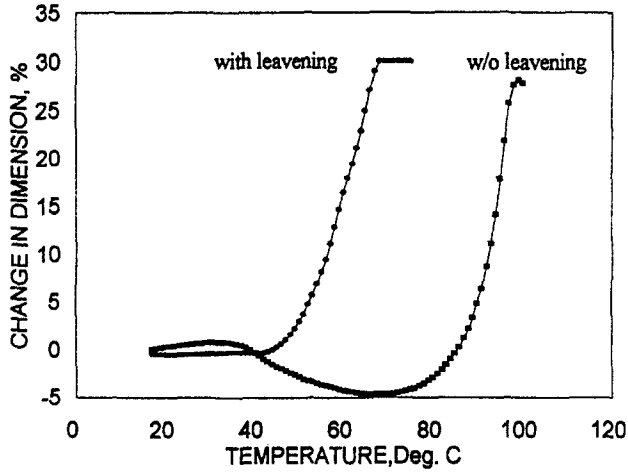

Fig. 2 TMA curves for cookie doughs made with soft wheat flour, 60% sugar, with and without leavening

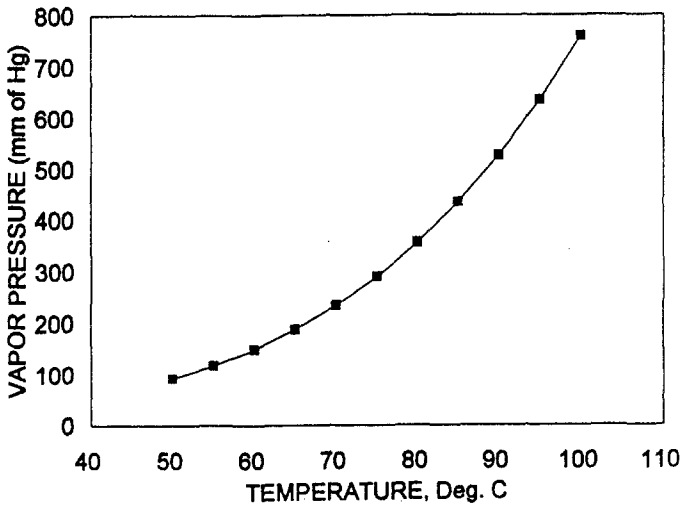

Fig. 3 Vapor pressure of water as a function of temperature

begin to expand with initial heating, rather than giving a biphasic TMA curve with a definite transition point. When water vapor pressure is plotted as a function of temperature, a curve with a different shape and no transition point is obtained (Fig. 3). The sugar in the dough system would lower the water activity and, thus, reduce the vapor pressure, which would shift the position of the curve but not change its shape.

We suggest that a possible explanation for the transition point in the TMA curve for cookie dough is that the gluten in the flour particles goes through an

apparent glass transition, thus gaining mobility that allows it to interact and form a web. The formation of this web increases the viscosity of the dough, and the dough can no longer spread under the force of gravity. The elongational viscosity of the cookie dough increased from 2.60×10^5 Pa.s at 30°C to 3.48×10^5 Pa.s (LSD 4.0×10^4) when the dough was heated to 80°C (above the transition point) and then cooled to 30°C. As the web forms, it decreases the rate of diffusion of water in the cookie dough, and thus, the dough retains water vapor, which results in the large increase in volume that is seen in the TMA curve.

Effect of flour type

Cookie dough made with hard wheat flour set at a lower temperature during baking and had a lower apparent T_g than did the soft-wheat-flour cookie doughs (Table 1). This is consistent with the suggestion of Doescher *et al.* [7] that cookie doughs made with hard wheat flour went through an apparent glass transition at a lower temperature. Doescher *et al.* [7] reported that, at constant moisture contents, the apparent glass transition of hard wheat flour, as measured by DSC, occurred at a significantly lower temperature than did that of soft wheat flour. This was not confirmed by the present TMA analysis. The apparent T_gs were identical (Fig. 4) for the soft and hard wheat flours at 13% moisture.

Effect of sucrose level

The level of sugar in the formula has been shown to affect final cookie diameter [15, 16]. Therefore, the sucrose level in the dough was altered to manipulate cookie diameter. The expansion of those cookie doughs was also measured in the TMA, to determine if sugar level affected the apparent T_g credited to the gluten proteins. The sucrose concentration affected cookie spread, as well as

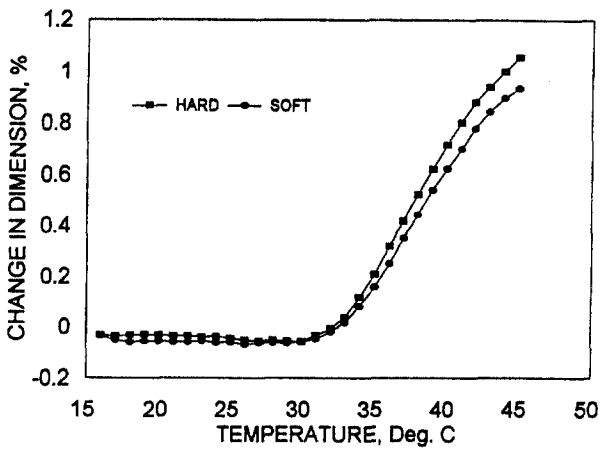

Fig. 4 TMA curves for hard wheat and soft wheat flours at 13% moisture

Table 1 Diameter, set time, and apparent T_g of dough for cookies baked with soft and hard wheat flours

Flour type	Diameter/ mm	Set time/ min	Apparent T_g/°C
soft	184	5.00	78
hard	161	4.75	71

Table 2 Effect of sucrose level on diameter, apparent dough T_g, and set time of hard and soft wheat cookies

Flour type	Sucrose/ %	Diameter[a]/ mm	Set time[b]/ min	Apparent[c] T_g/°C
soft	60	184 a	5.00 a	78 a
soft	50	171 b	4.75 ab	75 b
soft	40	159 cd	4.25 c	60 d
soft	30	148 f	3.50 d	66 e
hard	60	161 c	4.75 ab	71 c
hard	50	154 d	4.50 bc	69 d
hard	40	157 e	3.50 d	66 e
hard	30	139 f	3.00 e	64 f

[a] values followed by different letters are significantly different (LSD=3.74)
[b] values followed by different letters are significantly different (LSD=0.39)
[c] values followed by different letters are significantly different (LSD=1.41)

the set time and the apparent T_g (Table 2); both of the latter occurred at a lower temperature in cookie doughs made with hard wheat flour. Set time correlated highly with apparent T_g (r =0.971 for soft flour and r=0.989 for hard flour). The set time and apparent T_g of cookie doughs made with both flours increased as the sucrose level was increased, indicating that sugar delayed the set time.

Conclusion

The TMA appears to be an appropriate instrument to measure the apparent T_g of cookie doughs. However, such food systems must be heated at a slow rate (1 °C min^{-1}) to ensure experimental reproducibility, and steps must be taken to minimize moisture loss during measurement.

We suggest that the set time of cookie doughs is caused by an apparent glass transition of the gluten protein. As the gluten proteins go from glassy to rubbery, they form a web that retains water vapor in the dough. That retention of vapor is responsible for the large increase in dough volume seen in the TMA curve. The formation of the gluten web and its associated increase in viscosity

cause the cookie dough to stop spreading. Cookie doughs made with soft wheat flour went through an apparent glass transition at a higher temperature than did cookie doughs made with hard wheat flour. The difference in apparent T_g between cookie doughs made with hard and soft wheat flours was not an inherent property of the flour, but was affected by other factors in the system. Sugar concentration had a large effect on apparent T_g, presumably because of sugars poorer plasticizing effect, compared to that of water.

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