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Determination of glass transitions in boiled candies by capacitance based thermal analysis (CTA) and genetic algorithm (GA)

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ABSTRACT

The glass transition temperature (T_g) is an important property that influences the processing and textural characteristics of candy. Measurement of T_g is done by comparably expensive and complex instruments. In this study, we tested a new system which uses capacitance thermal analysis (CTA) of candy trapped between stainless plates, as the system is caused to heat at an uncontrolled rate. The data of capacitance as a function of temperature were processed by a genetic algorithm (GA), and fitted to a three-section model to determine T_g. T_g of the candies were independently measured by DSC as a reference. The results showed that when the T_g of the candy was below ~15 °C, the measurement from the GA-CTA was higher (2–3 °C) than that from DSC. However, if T_g of the candy was higher than 15 °C, the two methods gave similar values. GA based CTA provides a feasible new way to measure phase transitions in candies with relatively inexpensive equipment, and with less need for user interpretation of data.

1. Introduction

Candies, or sugar confections, are popular food products characterized by relatively high sugar content. This definition may encompass several distinctly different items such as chocolate, boiled sweets, and chewing gum. Confectionery foods are popular throughout the world and have been consumed for thousands of years. Some studies date the first production of candy to ca. 2000 BCE in ancient Egypt (Richardson, 2003). In the past, candies have served a medicinal role, as in the relief of sore throats, and were often only accessible to wealthy individuals. In the United States, sugar confections became more available to the general public in the 1830s. This coincided with the increase in sugar production in Louisiana and the West Indies, and the greater availability of cocoa beans. In addition, the industrial age had provided technological advances that allowed for mass production of sugary sweets. While the production and types of candies has increased since those times, much of the basic composition has remained much the same.

The texture, appearance, and storage stability are very importance factors which can influence consumer perception of candy. A unique feature of candies is that they can appear in many physical and structural forms, which in turn have a profound impact on their perceived texture. Candies containing only sugar (or glucose syrup) can manifest as chewy caramels or solid hard candies. The former are often present as rubbery states with no crystalline material, although graining or whipping may be used to create small sugar crystals that shorten the texture. Hard candies are usually produces as clear amorphous glassy states, although some confections such as rock candy may have sucrose crystals. Other confections incorporate gelling agents such as pectin to create very chewy products such as gummy bears and jelly beans. Of course a very prominent category of candy are chocolates. These contain fine dispersions of sugar and cocoa mass particles trapped in a solid fat phase.

The glass transition temperature (T_g) is one of the important factors that determines the physical properties of candies. A glassy state can be defined as an amorphous solid, or the amorphous portion of a semi-crystalline solid. Upon heating, the temperature at which a glassy solid transforms into a rubbery state is defined as the glass transition temperature (T_g). At temperatures below T_g, molecules exist in an amorphous solid with limited motion. At a macroscopic level, such materials are often clear and have a relatively hard, brittle structure. At temperatures above T_g, molecules can undergo rotational and translational movement in a 'rubbery' or liquid amorphous state. These materials can be fairly viscous or malleable, properties that influence the chewability of candies.

Controlling the physical states of candy is critical in the confection industry as desirable characteristics, texture, and storage stability are influenced by these states (Hartel et al., 2011). In

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general, food materials maintain better physical and chemical stability in the glassy state than in the rubbery state (Kumagai and Kumagai, 2002). Ergun et al. (2010) summarized some of the desirable states for confections, and indicated that hard candies should have a T_g which is much higher than room temperature, so that it can maintain its desired brittleness and hard texture over a range of ambient temperatures. Some other candies including ungrained caramels, chewy nougats, and marshmallows have a T_g lower than room temperature, thus exhibit a chewy texture.

To make glassy candies, both glass-formers and modifiers are needed. In addition, the candies need to be rapidly cooled down from a molten state so that crystals do not have time to form. The most common glass-formers are sugar (sucrose) and glucose syrup (Smidova et al., 2003). Other components such as maltodextrin, gum, color, and flavor serve either as glass-formers working to adjust the T_g of the candy glass, or as additives, changing the appearance and flavor. For most candy production, water is used as a plasticizer that can break down the network connectivity of glass-formers. Plasticizers lower the T_g by increasing the free volume in which molecules are free to move. The agents soften the material but may decrease chemical stability. Therefore, it is important to control the ratio of plasticizers to glass-formers, so that the candies can be made into desirable forms. Previous studies (Ergun et al., 2010; Tananuwong and Reid, 2004; Labuza and Labuza, 2004; Lourdin et al., 1997; Forssell et al., 1997) indicated that water content has great influence on the T_g, and lowering the water content of foods such as starchy materials, dried foods, confections, and frozen foods leads to a greater than linear increase in T_g. In addition, several studies (Bhandari and Howes, 1999; Roos and Karel, 1991a,b; Roos, 1993) have shown that the molecular weight of the primary glass-former has a major impact on T_g, with higher molecular weight compounds producing greater T_g values. The influence of the weight ratio of different components (glass-former and plasticizer) on T_g of food materials has been summarized by the Gordon-Taylor equation (Roos, 1995):

$$T_g = \frac{\omega_1 T_{g1} + k\omega_2 T_{g2}}{\omega_1 + k\omega_2} \tag{1}$$

where, ω_1 and ω_2 are the weight fractions of components 1 and 2 while T_{g1} and T_{g2} are the glass transition temperature of each component. The constant k is related to the difference in specific heat values for the two components between glass and fluid state ($k = \Delta C_{P1}/\Delta C_{P2}$).

Differential scanning calorimetry (DSC) is one of the most commonly used methods to determine glass transition temperatures. Thermodynamic transitions are classified as first- or second-order. In a first-order transition, there is a transfer of latent heat between system and surroundings, and the system undergoes an abrupt volume change. In a second-order transition, often called a continuous phase transition, there is no change in latent heat but the heat capacity does change. First-order transitions occur, for example, between the solid and melted states of crystalline sucrose. Glass transitions are second-order, as the greater motional freedom in the rubbery state give it a greater heat capacity than in the glassy state. In some systems, a material may undergo more than one glass transition, such as α and β relaxations. The DSC compares the relative heat flow of a sample and reference (such as an empty pan) during a linear temperature scan (Roos, 1995). The glass transition presents as a step in the heat-flow baseline. The change is not usually abrupt, but occurs over a temperature range. Thus, glass transitions are often characterized by onset, endset and midpoint temperatures (Hartel et al., 2011).

Another common approach to measure glass transitions is through rheological tests. Typically, this involves measurement of an elastic or viscous property as the sample temperature is gradually increased. This often involves small amplitude oscillations of the sample, with measurements of the phase lag between the stress and strain, from which the storage (E' or G') or loss (E'' or G'') moduli are derived. Generally, the oscillation frequency can be varied to mimic process conditions, or to adjust the relative stiffeness of the material. Cocero and Kokini (1991), Kasapis et al. (2003) and Madeka and Kokini (1996) measured rheological properties of different food materials over various temperature ranges, and found that at T_g there was a drastic drop of storage modulus G' and viscosity. In addition, a peak of loss modulus G'' appears when the samples reaches T_g. Other existing methods to determine T_g include dilatometry (Biliaderis et al., 1986), which measures the volume change during a temperature scan, and nuclear magnetic resonance (NMR) or electronic paramagnetic resonance (EPR), which measure the mobility of nuclei (mainly ^{1}H and ^{13}C) or spin probes (Ruan and Chen, 1997).

Yet another method for determining T_g is dielectric thermal analysis (DETA), which measures the variations of the dielectric constant as a function of temperature or frequency. This technique was demonstrated as particularly effective for the study of secondary relaxations in products with low water content (Champion et al., 2000). The typical DETA consists of parallel metal plates with a small gap between the plates to accommodate the sample being tested. As with DSC and thermal rheological methods, the sample temperature can be increased systematically as it moves from the glassy to rubbery states. The frequency dependence can also be investigated, typically over the range of 1 mHz–1 MHz, allowing researchers to determine different electrical properties that manifest at different frequencies (Räsänen et al., 1998). The instrument measures the stored electrical energy component (the dielectric constant ε') as well as that lost as heat (the dielectric loss ε''). As with dynamic rheological methods, the ratio tan δ ($\varepsilon''/\varepsilon'$) may help identify and characterize changes in material properties. The peak of tan δ that appears in some isochronal tan δ vs temperature plots is defined as T_g (Laaksonen and Roos, 2000). Some researchers have suggested that DETA is a more sensitive measurement than dynamic rheology, as often only one transition can be seen by rheological tests (Rotter and Ishida, 1992). As T_g measured by DETA varies substantially with frequency, it is important to specify and understand the measurement frequency before comparing results.

DSC, DETA and dynamic rheological thermal analyzers are relatively expensive instruments and require substantial user training to ensure reliable results. In addition, each require careful consideration of the data curves to determine T_g parameters, an exercise that may allow individual interpretations to bias the results. Thus, such approaches are often available only to large candy manufacturers.

The objective of this research was to construct and test a simple and relatively inexpensive device that could be used to measure glass transitions in candies. The device consisted of a parallel metal plate assembly to hold the sample, which was then frozen in a commercial freezer. The temperature of the sample was increased by bringing it to a constant temperature environment. While this does not allow linear increase in temperature, it greatly simplifies the instrument construction. As a measure of the increased mobility of molecules as temperature increased, the capacitance was monitored using an inexpensive capacitance meter. Capacitance is the ability of a subject to store electrical charge, and the capacitance of a parallel-plate capacitor can be determined as:

$$C = \varepsilon' \varepsilon_0 \frac{A}{d} \tag{2}$$

where ε' is the dielectric constant or permittivity of the sample