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Full Length Research Paper

Detection of dilution of milk with the help of glass transition temperature by differential scanning calorimetry (DSC)

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Glass transition temperature of pure milk, milk diluted with water, and pure milk in which sugars like glucose, fructose and sucrose were investigated by differential scanning calorimetry (DSC). The glass transition temperature T_g of pure milk (containing 89.2 kg water and 10.8 kg total solids per 100 kg milk) varied between -114 to -118 °C. Effect of change in composition of the milk varying the amounts of water and total solids content (77.47, 81.56, 83.81, 84.31, 85.76, 86.69, 89.43, 92.15, 93.16, 95.71 and 96.38 kg water to make each 100 kg milk sample) on the glass transition temperature of milk showed a linear relationship between glass transition temperature and composition of the milk expressed in %moisture content (w.b.). The addition of sugars (glucose, froctose and sucrose) also showed a significant change in glass transition temperature. Under applied conditions, adulterations in milk by dilution with water only and water and sugars were detectable even at 0.5 and 5 % respectively.

Key words: Milk, glass transition temperature, differential scanning calorimetry, adulteration.

INTRODUCTION

The term quality, as applied to milk and products made out of milk, embraces a variety of features. These include such diverse properties as absence of dirt, antibiotics, off-flavours, pathogenic organisms and abnormal numbers of body cells; evidence of cleanliness and care in production and handling as indicated by microbiological analysis; chemical analysis to check for dilution with water, removal of fat, and any added adulterants; possession of desirable aroma and flavor; and adequate amounts of those constituents which are of nutritional importance. The forms of adulteration like addition of water, skimming or removal of fat and addition of fluid skim milk can be detected from specific gravity and fat content (Singhal et al., 1997).

Glucose, cane sugar, urea, ammonium sulphate and other substances have been encountered as additives for the purpose of masking the effects of dilution of water. Even a sensitive test like freezing point of milk fails to unmask this adulteration (Dharmarajan et al., 1953). Density differences have been noted on addition of glucose, urea and ammonium sulphate, but again the increase in density is not exactly proportional to the molar concentration of the added solute. Also, rise in milk density due to glucose is greater than that due to urea and lower than that due to ammonium sulphate, and is not in molar proportions. So detection of such types of adulteration are generally based on composition and structure (molecular mobility) or physical properties measured by molecular refraction, differential thermal analysis, differential scanning calorimetry (DSC) or IR spectroscopy (Singhal et al., 1997; Kantor et al., 1999).

Most of the physical or chemical transformations involve heat exchanges. Therefore, DSC analysis has a very broad field of application. Even when no heat exchange occurs, as observed in glass transition, the phenomenon gives rise to a baseline deviation of the thermoanalytical curve, related to a variation of heat capacity. Glass transition and heat capacity measurements provide detailed information about both the physical and calorimetric properties of a substances

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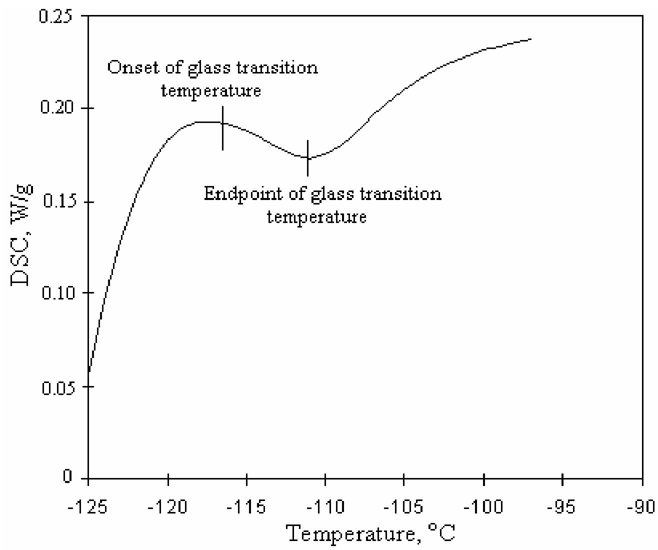

Figure 1. DSC thermograph for 87.5% moisture content (w.b.) sample.

(Bhandari and Howes, 2002; Laaksonen et al., 2001). The textural change of food materials is also measured with the help of glass transition temperature using DSC (Ross et al., 2002). The state diagram of date flesh was developed by measuring its freezing points, glass transition temperatures, maximal-freeze-concentration condition, and solute melting points by DSC (Rahman, 2004).

The glass transition of a polymer is described as a transition from a flexible rubber to a hard brittle solid (Shen and Eisenberg, 1966). For a low molecular weight material the glass transition is marked by an increase in viscosity of several orders of magnitude as the material is cooled from a super cooled liquid to a glass (Ollett and Parker, 1990; Truong et al., 2004). Glass transition temperature (T_g) is a terminology to characterize the transition from a liquid to a glassy state (or vice versa) of a substance. The onset or midpoint values of the transition in the thermographs are normally used for this terminology (Hawalkar, 1990). Glass transitions of food material have gained in importance in recent years, particularly in the case of dried and frozen products. Cordella et al. (2002) reported that Glass transition temperature variation is a powerful technique for characterizing the thermal behavior of honey and for detecting the effect of adulteration on physicochemical and structural properties of samples.

Considering that the detection of adulteration would require knowledge of the food products' physical and chemical properties, the approach of this present study followed two steps, firstly DSC was used to determine the thermal behavior of pure and diluted milk, and, secondly, DSC was used to analyze change in glass transition temperature due to addition of sugars like glucose, fructose and sucrose.

MATERIALS AND METHODS

Sample preparation

Milk of a commercial brand (Thacker Dairy, Midnapur an ISO 9001:2000 certified company) was purchased from a local market. According to the producer's specifications, the composition of milk was (for 100 ml.): 3.3 g milk fat, 3.0 g milk protein, 4.1 g lactose, 117 mg calcium, 88 mg phosphorus, 157 mg vitamin. So by calculation it was found that total milk solid was 10.8 / 100kg milk and water was 89.2 / 100 kg milk.

Moisture content of the milk was measured by using Mettler moisture analyzer (Mettler LJ16, 0.01). The sample was kept on the sample pan of the instrument and evaporation of moisture was carried out setting the temperature of the infrared-drying chamber of the instrument at 120°C. The moisture content was obtained as percentage moisture in wet basis.

Moisture content of milk at various levels was determined by vacuum oven (Annapurna Chemical Industries, Kolkata, ± 0.1°C and ± 1 mmHg) technique. The sample was kept on a Petri dish and evaporation of moisture was carried out overnight by setting the temperature at 65°C and vacuum level at 650 mm of Hg (AOAC. Official Methods of Analysis, 1997).

Milk solutions with different soluble sugars like glucose, fructose and sucrose were made by dissolving these solutes in the proportion of 5, 10, 15, 20, and 25% on the basis of milk weight. These solutions were maintained at the constant water content by adding the calculated amount of water externally.

Differential scanning calorimetry

A differential scanning calorimeter (DSC 204*Phoenix* Netzsch – Germany) was used for the calorimetric analysis of glass transition temperature. The purge gas used was dry nitrogen gas at a rate of 10 mlmin^{-1}. The protective gas for balancing the chamber used was also nitrogen gas at a flow rate of 20 mlmin^{-1}. Indium and Zinc (Netzsch standards) were used for temperature and flow calibration. Before measuring the Tg, the instrument was calibrated with two empty, closed Aluminium crucibles (Roos, 1995). One of the crucibles was used as the reference and the other was used for keeping the sample. About 20 - 25 mg of conditioned sample was taken in the sample crucible for the measurement of Tg. The sample was cooled to about -150°C and then heated to 40°C at 10°C min^{-1} heating rate (Jaya, 2002). The glass transition temperature was determined from the endothermic DSC thermograph as shown in Figure 1.

RESULTS AND DISCUSSION

Thermal behavior of milk with water

DSC thermographs were used to follow the effect of dilution of milk with water on the thermal behavior of milk. Lactose and water were the main constituents (>93%) of milk. Fat, protein, salt and minerals were minor constituents of milk.

In the DSC heating curve as shown in Figure 2. it is found that the glass transition temperature of milk decreases continuously with increase in water content. This gives a clear indication that this thermophysical property of the milk can be used as an indicator of adulteration of milk diluted with water. The glass transition temperture of pure milk varied from -114 and -118°C. Figure 2 indicates linear relationship between

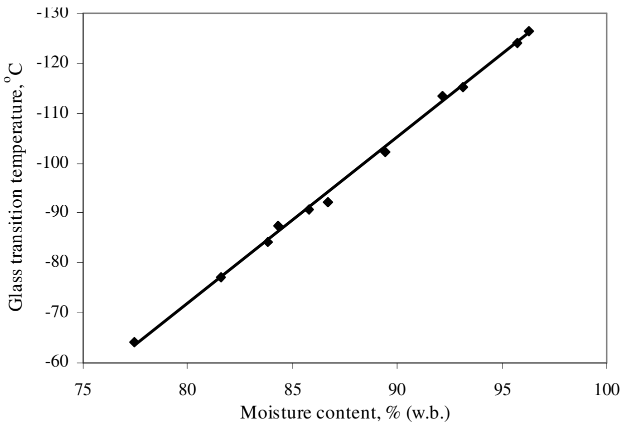

Figure 2. Glass transition Vs moisture content.

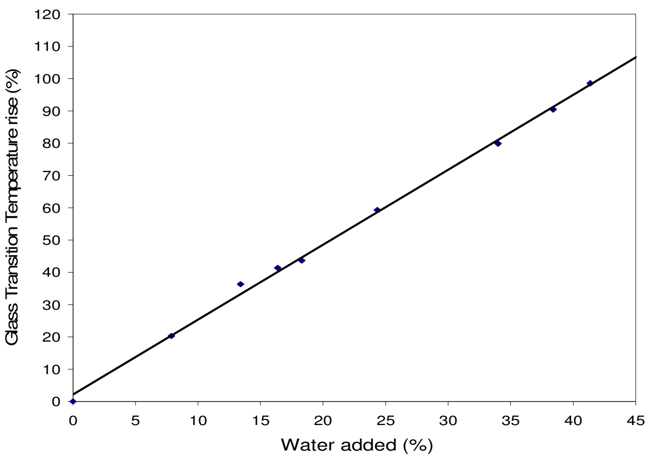

Figure 3. Rise in glass transition temperature by adding water.

Glass transition temperature and moisture content which is expressed as:

$$T_g = -3.3262\,M + 194.28 \qquad R^2 = 0.9977 \qquad (1)$$

where M is the moisture content on wet basis of milk and R^2 is the coefficient of determination of the tendency curve. It is clear from the eq.(1) that the addition of water was detected by statistically significant temperature gap. From curve fitting a direct relationship for calculatiing the added water percentage was found out by knowing the rise in the glass transition temperature. The equation is:

$$\Delta Tg = 2.332A + 2.1429 \qquad R^2 = 0.9978 \qquad (2)$$

where A is the percentage of water added and ΔTg is the rise in glass transition tamprature in percentage. The adulteration of milk diluted with water was detectable at a dilution level of even 0.5% (The minimum difference in change of water content between two successive levels

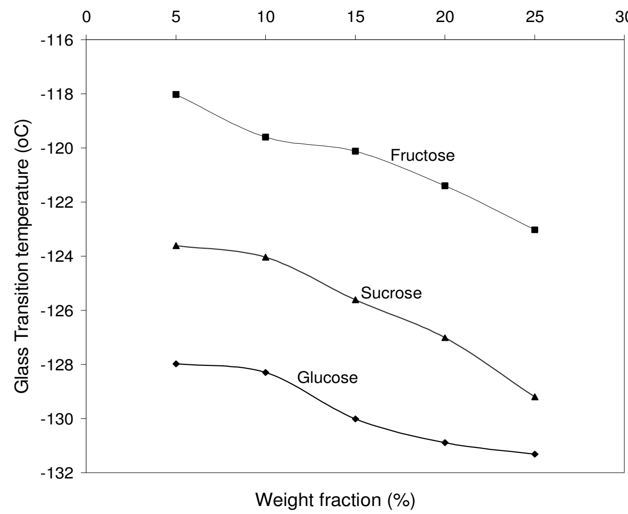

Figure 4. Tg vs. Weight fraction of sugar added in milk.

of 84.81 and 85.31%). Table 1 illustrates the glass transition temperature at different composition of milk with respect to moisture content and total solids.

Thermal behavior of milk with dissolved sugars

When the DSC thermographs of milk were analyzed at different weight fraction of fructose having T_g = 4.8°C, maintaining the constant weight fraction of water, its glass transition temperatures were found to vary between -118.02 and -123.02°C. It is clear that the change in Tg with weight fraction of fructose is very small as shown in Figure 4.

Almost similar type of phenomenon was depicted by glucose and sucrose. In case of glucose having T_g = 31.5°C, and sucrose having T_g = 58.5°C, glass transition temperature varied from -127.97 to -131.31°C and -123.61 to -129.2°C respectively. But with glucose, it was found that the values of glass transition temperature attained almost a constant value with increased amount of weight fraction. At the same time in case of fructose and sucrose Tg decreased continuously. Since the difference between the additions of two successive sugars to the milk samples was 5%, the adulteration in milk by sugars could be measured at a minimum impurity level of 5%. Similar results were obtained by researchers in case of honey (Cordella et al., 2002; Kantor et al., 1999).

Conclusion

Glass transition temperature is one of the most potentially useful parameter powerful for characterizing the thermal behavior of milk and for detecting the effect of adulteration on physicochemical and structural properties of milk.

In the DSC heating curve it was found that the glass transition temperature of milk rose continuously with de-

Table 1. Glass transition temperatures of milk with various composition.

Sl. No.	Water content (kg/100 kg milk)	Total solids (kg/100 kg milk)	Glass transitiontemperature, T_g (°C)
1.	77.47	22.53	-64.1
2.	81.56	18.44	-77.1
3.	83.81	16.19	-84.2
4.	84.31	15.69	-87.4
5.	85.76	14.24	-90.6
6.	86.69	13.31	-92.1
7.	89.43	10.57	-102.1
8.	92.15	7.85	-113.5
9.	93.16	6.84	-115.3
10.	95.71	4.29	-124.2
11.	96.38	3.62	-126.6

crease in water content, which gave a clear indication that this thermophysical property of the milk could be used as an indicator of adulteration of milk by the dilution of water. So the addition of water could be detected by statistically significant temperature gap, which was 4.4779°C for 1% added water. When soluble sugars like glucose, fructose and sucrose were added, it caused inevitable changes in Tg due to implicit structural modification and change in composition. So these sugars can not be used for hiding the milk adulteration by dilution of milk with water. The observed effect could be used for developing a new technique for detection of dilution of milk.

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