Glass Transitions in Frozen Sucrose Solutions

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ABSTRACT

Dynamic Mechanical Analysis, DMA was used to study glass transitions in frozen sucrose/guar solutions. The glass transition temperature, T_g, decreased with increased sucrose content in the sample. Guar gum did not influence T_g. The module was, however, strongly dependent on the mechanical properties of guar gum. Changes in sample dimensions provided useful information about the crystalline phase.

INTRODUCTION

The interest in the glassy state in foods has increased steadily in the last ten years. The glassy state in frozen foods has been widely studied since it affects food stability.
It has been shown earlier that the storage temperature strongly influences the shelf life of the product. Low temperature causes high viscosity and low diffusion rate in the product. The result is slow chemical and enzymatic reactions in foods during storage at low temperatures. Now it is known that another factor also influences the storage stability, the glassy state[1]. Above the glass transition i.e. in the liquid or rubbery state, solutions or foods are unstable and reactive. Ice crystallization can also occur in this phase. Below the glass transition temperature the material becomes glassy and no molecular motions or chemical reactions occur. The ice crystallization is prevented and the shelf life of the product is prolonged.

Ice cream is a product which suffers deleterious effects such as ice crystal growth and structural collapse during storage. In order to prevent such effects polysaccharides are added. The influence of polysaccharides on the mechanical properties in ice cream and frozen sucrose solutions has been studied by Goff et al.[2] and Blond[3].

In this study Dynamic Mechanical Analysis, DMA was used to investigate glass transitions in frozen sucrose solutions. In DMA the mechanical properties of a viscoelastic material are measured when the sample is subjected to a small oscillatory force.

The purpose of this study was to further investigate the mechanical properties of frozen sucrose solutions and to examine the influence of guar gum added to the solutions. Does guar gum influence the mechanical properties and T_g of the sucrose solutions? Finally, the mechanical properties of a commercial sorbet was investigated and compared to the model solutions.

MATERIAL AND METHODS

Purification of guar gum

Guar gum from Sigma Chemical Company was dissolved in distilled water at 1.5 % w/w and 30°C in order to separate impurities from the polysaccharide. The insoluble impurities were separated from the guar solution by centrifugation at 12 000 rpm for 1 hour. The guar solution was then freeze-dried for five days.

Sample preparation

Solutions were prepared with different sucrose and guar concentrations. Sucrose and guar were dissolved in distilled water at 70°C.

DMA measurements

DMA measurements were carried out using an RSA II (Rheometrics, Piscataway, USA). The sample is subjected to a sinusoidal, non-destructive deformation. From the sample response the storage modulus, E´, and the loss modulus, E´´, are calculated. The test sample was placed between two parallel plates and the height was adjusted so that the sample was held between the plates by capillary forces. Air cooling was used to obtain temperatures between 20°C and -65°C. Measurements were made during cooling and heating with a rate of 1°C/min.

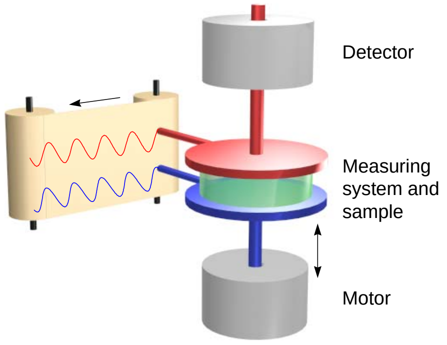

Figure **Fel! Okänt växelargument.**. The principle of DMA.

RESULTS AND DISCUSSION

The DMA result for a sample with 14 % sucrose and 1 % guar is shown in figure 2. During cooling from 20°C the storage modulus is about 10^4 Pa. At the crystallization temperature the modulus immediately increases to 10^7-10^8 Pa. This step occurs at -14°C and is probably a result of supercooling. The mixture has only a small contribution of amorphous sucrose due to the high water content. However, a glass transition was observed by the maximum in E” at -32°C (during cooling).

On heating some differences were observed compared to the cooling treatment. The step in the storage modulus occurs at higher temperature than on cooling i.e. there is a hysteresis phenomenon. The storage modulus falls over a broader temperature interval, compared to the step at -14°C on cooling. In comparison to a pure 20 % sucrose sample, E´ and E´´ are more than 10 times higher in the sample containing both sucrose and guar gum at temperatures above T_g.

DMA measurements also provide information about changes in the sample height (ΔL) which is equal to the plate to plate distance. The volume of water will expand when it reaches its freezing point and crystallizes. A semicrystalline sample will also expand proportional to the amount crystallizing water. Even the sample containing 85 % water shows a clear step in ΔL at -14°C during cooling, see figure 2. When cooled further ΔL decreases below its original height.

In the solution containing 69 % sucrose and 1 % guar, shown in figure 3, there seems to be no crystallization at all. The storage modulus increases over the whole cooling

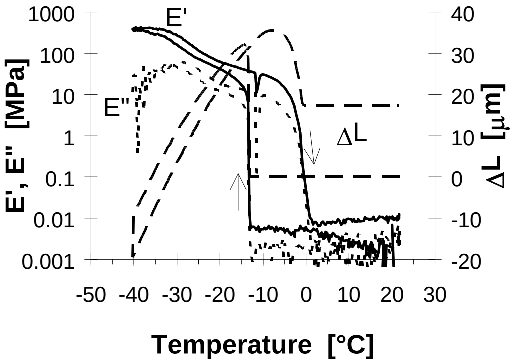

Figure **Fel! Okänt växelargument.**. DMA results for a solution with 14 % sucrose and 1 % guar gum.

cycle scan and represents a typical glass transition. This could also be seen in the variation of ΔL. When cooled, the sample height decreases and no peak corresponding to crystallization occurs.

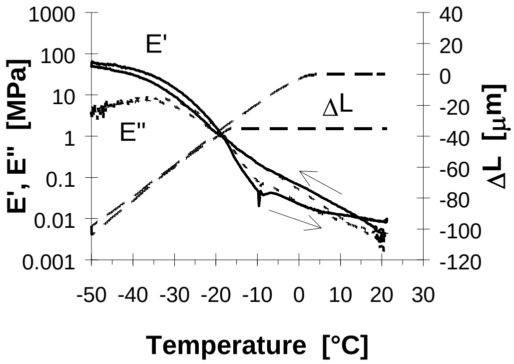

Figure **Fel! Okänt växelargument.**. DMA results for a solution with 69 % sucrose and 1 % guar gum.

The investigation of sorbets containing about 20 % sucrose, shown in figure 4, shows similar behaviour to the sample with 14 % sucrose and 1 % guar gum. During heating, two peaks were observed in the glass transition region. The first corresponds to T_g, the second to the melting of ice.

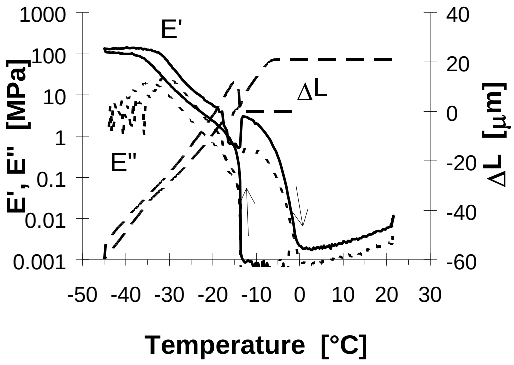

Figure **Fel! Okänt växelargument.**. DMA results for lemon sorbet with about 20 % sucrose.

Changes in sample volume during the cooling process can be described by the parameter $Cr = \Delta L_{peak}/L_0$, where ΔL_{peak} is the thermal expansion caused by crystallization and L_0 is the original height of the sample, see figure 5. In a semicrystalline sample ΔL will increase at the freezing point (which is equal to the temperature of crystallization), but further cooling will cause a decrease in ΔL. The magnitude of the step in ΔL depends on the water content. Samples with high water content will show a larger step in ΔL than a sample with low water content.

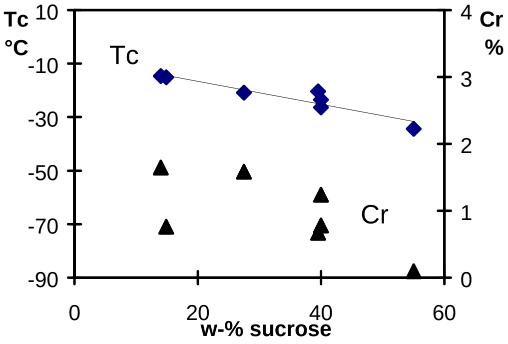

Figure **Fel! Okänt växelargument.**. Degree of crystallinity, Cr (%), and temperature of crystallization, T_c at different sucrose concentrations.

The temperature where the ΔL step occurs will decrease when the concentration of sucrose increases as shown by T_c in figure 5. In a dilute sucrose solution the water molecules can rather easy form ice crystals, but when the sucrose concentration is high the water molecules are hindered by the sucrose molecules. This could explain the decreased crystallization temperature with increased sucrose concentration.

Sucrose-Tg relations

The glass transition temperature, T_g, seems to decrease as the concentration of sucrose is increased. The T_g values in figure 6 comes from the cooling treatment, but similar results are obtained on heating.

Pure sucrose samples also showed similar results, i.e. the addition of guar gum did not affect T_g. The standard deviation for the 39.5 % and 55 % sucrose samples are shown by error bars in figure 6 as an example of the scatter.

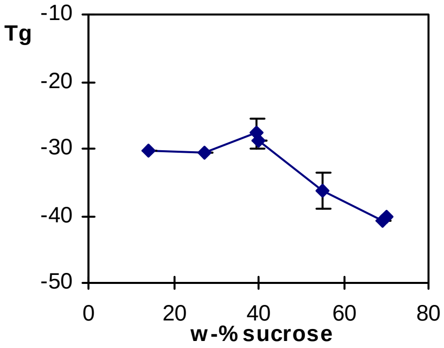

Figure **Fel! Okänt växelargument.**. Tg (°C) as a function of sucrose in sucrose/guar containing samples.

When a sugar or aqueous polymer solution is cooled, all accessible water will not crystallize as ice during the first cooling process. To convert a maximum amount of water to ice, an annealing treatment is necessary[4]. When the sample is cooled and heated several times a maximally freeze-concentrated fraction is obtained and maximum amount of water will crystallize. The amorphous freeze-concentrated phase corresponds to a glass transition temperature higher than in a sample without annealing treatment. Without cycling the temperature, the amorphous fraction contains more water which has a plastizicing effect on T_g. This could explain the lower T_g at 55 % and 70 % in figure 6.

CONCLUSION

The glass transition temperature decreases as the sucrose concentration increases.

Guar gum does not influence T_g when added in small amounts (<1 %). The module of the solution is, however, strongly dependent of the mechanical properties of guar gum.

The ΔL step and the temperature were the ΔL step occurs, will decrease as the sucrose concentration increases.

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