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Determination of glass transition temperature of beef and effects of various cryoprotective agents on some chemical changes

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ABSTRACT

Sucrose (2%), sorbitol (2%), mannitol (2%), gum arabic (0.15%), carrageenan (0.15%) and meat stabilizer (0.5%) were blended with ground beef and stored for 6 months separately at −9 °C, −13 °C (glass transition temperature (T_g) of beef determined by Differential Scanning Calorimetry (DSC)) and −18 °C. Total volatile basic nitrogen (TVB-N) and Thiobarbituric acid-reactive substances (TBARS) were determined at 1, 3 and 6th months of storage. Cryoprotectants and storage period had a significant effect ($P < 0.05$) on the TVB-N and TBARS values. Although there were no statistically significant differences between storage at −13 °C (T_g) and −18 °C, storage at −9 °C had different effects on TVB-N and TBARS.

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1. Introduction

Recently, the limitations of water activity (a_w) on food stability have been underlined and several alternatives have been proposed. One of these is use of the glass transition since it has been proposed that this transition greatly influences food stability, as the water in the concentrated phase becomes kinetically immobilized and therefore does not support or participate in reactions (Rahman, 2006).

Research on beef T_g is limited, and with the exception of those reported by Levine and Slade (1989), and Brake and Fennema (1999a) the values are inexplicably low (−40 °C to −60 °C). For beef, reported values are −60 °C (Rasmussen, 1969), −40 °C (Simatos, Faure, Bonjour, & Couach, 1975), >−5 °C (Levine & Slade, 1989), and −12 °C (Brake & Fennema, 1999a).

Although frozen foods are microbiologically stable, they are prone to chemical and physical (e.g. recrystallization, moisture migration) deterioration during storage. Procedures for accurately predicting the stability of frozen foods do not exist. It has been suggested that improved long-term storage stability of food could be achieved by storing food in a frozen amorphous glassy state, where the molecules from a non-periodic and non-symmetric network presumably resulting in an extremely high viscosity and thus the molecules are immobilised. Because of this very limited molecular motion, a food product in a glassy state is assumed not to deteriorate during storage (Orlien, Anderson, Jouhtimaki, Risbo, & Skibsted, 2004). However, the possibility that transition of the food system into glassy state may not be sufficient to limit molecular motions has recently been suggested (Champion, Le Meste, & Simatos, 2000; Le Meste, Champion, Roudaut, Blond, & Simatos, 2002; Orlien et al., 2004).

Chemical reactions are a major cause of frozen food deterioration and the T_g approach is the only potentially reliable measure for predicting chemical stability of foods at subfreezing temperatures. The quality loss of stored meat and meat products could be mainly due to lipid oxidation and protein degradation. Lipid oxidation is a major cause of frozen food instability, and muscle tissues are especially susceptible to this mode of deterioration. It should, therefore, be informative to study oxidation and hydrolysis of lipids in muscle tissue, giving special attention to changes in the rates of these reactions at temperatures around T_g. It is currently not known whether these reactions would be diffusion limited or not (Brake & Fennema, 1999b).

Addition of biopolymers to food systems could increase T_g, and they can therefore be stored at higher temperatures with greater stability and longer storage life with respect to diffusion limited reactions (Herrera, Pastoriza, Sampedro, & Cabo, 1999). The physical mechanisms of cryoprotection by biopolymers are not fully understood. Despite the fact that some evidence supports this contention, it is difficult to find much research in this area and thus, studies to determine the effects of an added biopolymer on the temperature dependence of reaction rates is needed.

The objectives of this study were: (1) to determine the T_g value of beef using DSC, (2) to determine the temperature and storage

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time dependence of the rates of oxidation of lipids and partial protein degradation in frozen ground beef with and without different cryoprotectants.

2. Materials and methods

2.1. Source of meat and chemicals

Meat samples were obtained from the *Longissimus dorsi* muscle of middle age Eastern Anatolian Red beef carcasses from a major slaughter-house (Et ve Balık Kurumu Kombinası, Erzurum, Turkey). After slaughter, carcasses were chilled for 24 h in a cooling room. Following chilling, all trimmable fat and connective tissue were removed.

Sucrose, sorbitol, gum arabic were provided by Fluka Chemia, mannitol by Cargill, and κ-carrageenan by Incom (Incom A.Ş. Mersin, Turkey).

2.2. Sample preparation

Meat samples were ground once through a 3-mm plate, and then mixed separately with cryoprotectants (sucrose 2%, sorbitol 2%, mannitol 2%, gum arabic 0.15%, κ-carrageenan 0.15% and meat stabilizer 0.5% w/w) for 2 min using a Hobart chopper. Each ground beef sample (75 g) with and without the addition different cryoprotectants were vacuum packaged and stored for 24 h at 4 °C to allow cryoprotectant diffusion and then frozen at −40 °C. The frozen meat samples were stored at −9 °C, −13 °C and −18 °C for the periods of 1, 3 and 6 months. After different storage periods the samples were taken for analyses.

2.3. Measurement of T_g by DSC

T_g value was determined by DSC (DSC-50, Shimadzu Corporation, Kyoto, Japan) equipped with a low temperature cooling unit (LTC-50, Shimadzu Corporation, Kyoto, Japan). The DSC was calibrated using mercury and indium standards, with onset temperatures of −38.87 °C and 156.6 °C, respectively. Beef samples (approximately 10 mg) were weighed into aluminum DSC pans, hermetically sealed, and then loaded onto the DSC instrument at room temperature, using an empty pan as a reference. Samples were then cooled at 5 °C/min to −80 °C, held for 15 min, warmed up to the annealing temperature, held for 1 h, re-cooled to −80 °C at 5 °C/min, held for 15 min and then scanned at 5 °C/min to 20 °C. T_g is reported as the mid point of the step.

2.4. TVB-N

TVB-N was determined using the procedure described in Anonymous (1988). The results were expressed as mg TVB-N/100 g.

2.5. TBARS

TBARS values for lipid oxidation was determined according to Lemon (1975). The TBARS values were expressed as μmol TBARS per kg meat.

2.6. Statistical analysis

This data was analysed according to completely random block design with three replicates. A one-way analysis of variance (ANOVA) was performed to test significances among treatments. Data were analyzed with the SPSS (SPSS, 2004). The Duncan's multiple comparison tests were used to separate mean differences.

3. Results and discussions

3.1. T_g value of beef sample

A typical thermal curve of beef heated from −80 °C to 20 °C with annealing is shown in Fig. 1. DSC results revealed two characteristic thermal events: the glass transition and ice melting. The T_g value of beef was determined as −13 °C from DSC curves. This value is close to the value reported by Brake and Fennema (1999a).

3.2. TVB-N

The results of variance analysis for TVB-N showed that the type of cryoprotectant, the storage temperature and the storage period were statistically significant ($P < 0.01$).

Except for mannitol, addition of cryoprotectants caused a decrease in the TVB-N value compared to the control (Table 1). These results showed that the best cryoprotectant for beef was gum arabic during the frozen storage. By adding cryoprotectants to food systems, their T_g could increase and they can, therefore, be stored at higher temperatures with greater stability and longer storage life (Herrera et al., 1999). The stabilizing effects associated with stabilizers have been widely explained by preferential interaction and the glass transition. The preferential interaction involves preferential interaction of protein with water rather than stabilizers, which are preferentially excluded from the proteins hydration shell, thus, unfolding of protein is prevented and its native conformation is stabilized (MacDonald & Lanier, 1991; Ohkuma et al., 2008). The reason why the lowest values are in the samples with gum arabic is probably due to a gel of gum arabic forming. If biopolymer can form a gel, as gum arabic and carrageenan can, they may aid in the formation and retention of small ice crystals and prevent ice growing into the network. In addition, the gel may hinder mutual contact, hence sintering of ice crystals (Walstra, 2003).

The effect of storage temperatures on TVB-N values are shown in Table 1. As can be seen, significant differences were found for TVB-N values at different storage temperatures. TVB-N values of samples at −9 °C were significantly different to those −13 °C and −18 °C ($P < 0.05$). The lowest TVB-N values were at −18 °C while the highest values were at −9 °C. These results are ascribed to the glass transition as Rahman (2006) reported that the food is stable at and below its glass transition whereas its deterioration is higher above the glass transition. In addition, at the T_g, the viscosity of amorphous materials becomes high, and the molecular mobility is lower (Lievonen & Roos, 2002; Roudaut, Simatos, Champion, Contreras-Lopez, & Le Meste, 2004).

Storage period significantly affected TVB-N values ($P < 0.05$, Table 1). TVB-N values increased with increasing frozen storage time. This may be attributed to increased protein degradation during the storage.

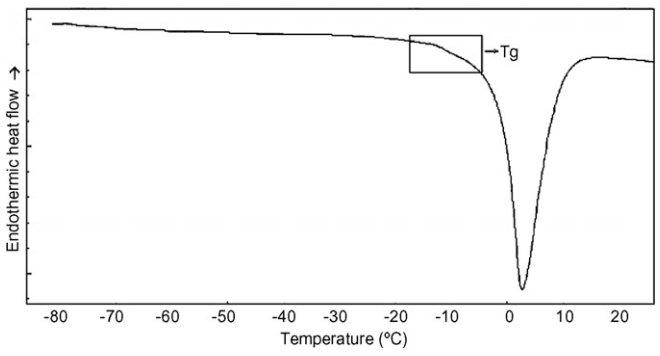

Fig. 1. Representative DSC curve of beef and the region of T_g.