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Effect of Various Biopolymers on Glass Transition Temperature of Chicken Breast Meat

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ABSTRACT

In this study, glass transition temperatures (T_g) as well as ice crystallization and melting temperatures and enthalpy values were determined by using Differential Scanning Calorimetry (DSC) for chicken breast meat samples blended with different levels (2, 4, and 8%) of xanthan gum, κ-carrageenan and gum arabic. The water activity (a_w) values, moisture contents and unfreezable water fractions of the samples were also analyzed. While the moisture contents decreased and unfreezable moisture fractions increased, the a_w values of the samples unchanged by addition of the biopolymers. The ice crystallization enthalpies and melting temperatures and enthalpy values decreased with increased levels of biopolymer additions. T_g value of the chicken breast meat was detected as -17.08±0.04°C (midpoint). It was observed that T_g values of the samples significantly affected by the biopolymer addition (P<0.01) and increased for the samples including 4% and %8 xanthan gum and 8% κ-carrageenan.

Keywords: Chicken meat, Glass transition, Gum, Carrageenan, Unfreezable water

Tavuk Göğüs Etinin Camsı Değişim Sıcaklığı Üzerine Bazı Biyopolimerlerin Etkisi

ÖZ

Araştırmada, farklı oranlarda (%2, 4 ve 8) ksantan gam, κ-karragenan ve gam arabik ilave edilen tavuk göğüs eti örneklerinin camsı değişim sıcaklıkları (T_g) ile kristalizasyon ve erime sıcaklıkları ve entalpi değerleri Diferansiyel Taramalı Kalorimetre (DSC) cihazı kullanılarak belirlenmiştir. Ayrıca örneklere ait su aktivitesi (a_w) değerleri ile nem içerikleri ve dondurulamayan su fraksiyonları da tespit edilmiştir. Biyopolimerlerin ilavesiyle örneklerdeki nem içeriğinin azaldığı, dondurulamayan su fraksiyonunun arttığı, a_w değerlerinin ise değişmediği gözlenmiştir. Örneklere ait kristalizasyon entalpileri ile erime sıcaklıkları ve entalpileri ise ilave edilen biyopolimer oranı arttıkça azalmıştır. Araştırmada, tavuk göğüs eti için T_g değeri -17.08±0.04°C olarak (orta nokta) belirlenmiş olup, T_g değerinin biyopolimer ilavesinden çok önemli seviyede (P<0.01) etkilendiği, %4 ve %8 ksantan gam ve %8 κ-karragenan ilave edilen örneklerde ise artış gösterdiği tespit edilmiştir.

Anahtar Kelimeler: Tavuk eti, Camsı değişim, Gam, Karragenan, Dondurulamayan su

INTRODUCTION

The poultry industry performed tremendous growth in the late 20th century, and this growth has been continued in the new century. Chicken meat may be the most universally accepted and consumed meat in the World with their taste and nutritive value [1-3]. Also, different chicken meat products are produced and consumed in recent years. However, the safety of these products is of major concern to its manufactures as well as end users [4]. In this context, freezing is one of the most important and widely used preservation techniques in meat industry. However, the stability of frozen meat depends on the state of water in the product and the stability of ice crystals during frozen storage [4, 5]. Hence the formation of glassy state, and glass transition concept are very much relevant during frozen storage [6]. It is pointed that the water activity concept is insufficient to predict shelf stability of frozen foods and some complementary ideas like storing meat below glass transition temperature (T_g), may help to improve the shelf stability [4]. According to Rahman [7, 8] there are two main rules of glass transition concept: (i) the food is most stable at and below its glass transition, and (ii) higher the T-T_g (i.e above glass transition), higher the deterioration or reaction rates.

Phase transitions in foods can be divided into two groups: First and second order phase transitions. At the first order transitions, such as melting, crystallization or evaporation, the physical state of a material changes isothermally from one state to another by release or absorption of latent heat; however, a second-order transition, such as amorphous state to glassy state, occurs without release or absorption of latent heat [8, 9]. Glass transition is a second-order and time-temperature dependent transition, which is characterized by a discontinuity in physical, mechanical, electrical, thermal, and other properties of a material [7]. Glass transition occurs when a super-cooled, malleable liquid/rubbery material is changed into a disordered solid glass upon cooling or vice versa [10]. Levine and Slade [11] and Slade and Levine [12] claimed that T_g influences the stability of foods. The hypothesis has recently been stated 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 [6, 8].

Glass transition can be influenced by heating/cooling rate, pressure and molecular weight as well as composition of the food material, especially water content. The molecular weight of any food material strongly influences T_g values. Low molecular weight polymers and monomers in their pure form have a low T_g whereas longer chain molecules have higher T_g [13]. It is reported that increasing the molecular weight or the cross-link density for a given polymer will decrease its specific volume, resulting an increase in T_g [14]. Thus the addition of any additive with high molecular weight in food can increase the T_g value. 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 [15].

There are several published values for T_g of beef and various fish species [16-26]. However there are only few studies about the T_g of chicken meat [2, 4]. The objective of this study was to determine the effect of various biopolymers (κ-carrageenan, gum arabic and xanthan gum) on the T_g values of chicken breast meats.

MATERIALS and METHODS

Sample Preparation

Chicken breast meat was bought from a local market. After all trimmable fat and connective tissue were removed, the meat was ground once through a 3-mm plate and then mixed separately with biopolymers (κ-carrageenan, gum arabic or xanthan gum (Sigma-Aldrich, Inc., St. Louis, Missouri, USA)) at the levels of 2%, 4% and 8% (w/w) for 2 min using a laboratory type mixer (Waring 8011 EB Blender, Stamford, USA). Each sample (100 g) with and without the addition of different biopolymers were vacuum packaged in PA/PE bags and stored for 24 h at 4°C to allow biopolymer diffusion and then frozen at -40°C. Before the experiments, the meat samples were thawed in a refrigerator at 4±1°C for 12h.

Water Activity (a_w)

Water activity values of the samples were determined with a TH-500 a_w sprint apparatus (Novasina TH-500, Lachen, Switzerland). The system was calibrated with six different salt solutions at 25°C before use. The samples were placed into plastic containers supplied by the manufacturer and then located into the measuring cabinet of the device at 25°C for determining a_w values.

DSC Measurements

Measurements were carried out with Differential Scanning Calorimetry (DSC-60, Shimadzu Corporation, Kyoto, Japan). The DSC was calibrated for temperature and heat flow with indium ($mp = 156.60℃, \Delta H_m = 28.45\,J/g$), distilled water ($mp = 0℃, \Delta H_m = 335\,J/g$) and heptane ($mp = -91℃, \Delta H_m = 140\,J/g$). Meat samples (approximately 10 mg) were weighed into aluminum DSC pans, hermetically sealed, and then loaded onto the DSC instrument at room temperature. An empty pan was used as reference, liquid nitrogen poured into the cooling can of the DSC instrument was used as coolant, and nitrogen gas at a flow rate of 50ml/min was employed in the purge line to control the local environment around the sample. The samples were then cooled at 5°C/min to -80°C, held for 15min, warmed up to the annealing temperature, held for 1h, re-cooled to -80°C at 5°C/min, held for 15min and then scanned at 5°C/min to 20°C. The analysis of the glass transition reports the onset, mid-point and endset temperatures of the step once the start and stop points of the transition are provided. The melting and crystallization temperatures (onset, peak and endset) were also detected from the obtained thermograms.

Thermogravimetric Analysis (TGA)

Thermogravimetric analyzer (TGA-50, Shimadzu Corporation, Kyoto, Japan) was used to determine the accurate moisture content in all the samples by plotting percentage weight loss against time under a controlled atmosphere. Initial weight of each sample was approximately 20 mg. Samples were placed in platinum pans and heated in a furnace flushed with N_2 gas at the rate of 50 mL/min and heated from 20°C to 105°C at a rate of 10°C/min and held isothermally for 60min [4].

Determination of Unfreezable Water

The unfreezable water mass fraction could be calculated from the difference between total water content and the amount of melted ice detected by DSC fusion endotherm. The expression (Eq. 1) is presented as follow:

$$W_u = W_t - \left(\Delta H_f / \Delta H_w\right) \qquad \text{(Eq. 1)}$$

where W_u is the unfreezable water mass fraction (%), W_t is the total water content (%), ΔH_f and ΔH_w are the enthalpy of water fusion (J/g) and latent heat of fusion (J/g) respectively.

Statistical Analysis

This study was conducted according to completely randomized design with three replicates. A one-way analysis of variance (ANOVA) was performed to test significance among treatments. Data was analyzed with the IBM SPSS Statistics 20 packed program. The Duncan's multiple comparison tests were used to separate mean differences.

RESULTS and DISCUSSION

Water Activity Results

The concept of water activity has been used conventionally to study the stability of food products. It has provided a reliable assessment of microbial growth, lipid oxidation, nonenzymatic and enzymatic activities in foods [27]. In this study, it was observed that a_w values for all the samples were between 0.986-0.989 and the biopolymer use had insignificant effect on the a_w values of the samples (P>0.05). It was claimed that the concept of water activity alone is insufficient to predict shelf stability of frozen foods and the alternate complimentary ideas like storing meat below T_g, may help to improve the shelf stability [4]. Studies indicated that the concept of T_g should be added along with the existing concept of water activity, to get a better understanding about the factors governing the stability of foods [18, 28, 29].

DSC Results

Ice crystallization and melting are the first order phase transitions occurred at a temperature range by release or absorption of latent heat during the cooling or heating. The ice crystallization and melting temperatures and enthalpies of the samples were measured by DSC. The results of the ice crystallization of the samples are summarized in Table 1.

Table 1**.** Effect of biopolymers on ice crystallization temperatures and enthalpies of chicken meat samples

Biopolymer	Ratio (%)	Temperature (°C)						Enthalpy (J/g)	
		Peak	Mean	Onset	Mean	Endset	Mean	ΔH	Mean
Control	-	-7.61±0.24[a]	-7.61±0.24[a]	-11.83±0.89[a]	-11.83±0.89[a]	-15.61±0.41[a]	-15.61±0.41[a]	193.89±2.01[a]	193.89±2.01[a]
	2	-8.23±1.76[a]		-12.59±2.87[a]		-16.10±2.13[a]		187.00±4.70[ab]	
κ-Carrageenan	4	-7.25±0.38[a]	-7.69±0.10[a]	-8.89±0.95[a]	-10.74±2.21[a]	-14.25±0.83[a]	-15.14±1.42[a]	182.56±1.14[bc]	178.86±9.49[b]
	8	-7.59±0.05[a]		-10.72±0.20[a]		-15.06±0.44[a]		167.03±2.66[d]	
	2	-7.17±0.21[a]		-9.97±0.26[a]		-14.89±0.21[a]		186.10±4.63[abc]	
Xanthan gum	4	-8.44±1.86[a]	-7.68±1.12[a]	-13.13±3.46[a]	-10.63±2.75[a]	-16.82±2.53[a]	-15.36±1.74[a]	179.08±5.18[c]	176.22±11.55[b]
	8	-7.44±0.46[a]		-8.77±1.74[a]		-14.38±0.82[a]		163.49±9.12[d]	
	2	-7.23±0.54[a]		-9.93±0.89[a]		-14.71±0.66[a]		188.83±2.65[ab]	
Gum arabic	4	-7.40±0.43[a]	-7.50±0.46[a]	-10.29±1.44[a]	-10.60±1.14[a]	-14.96±0.99[a]	-15.18±0.81[a]	183.97±3.24[bc]	180.49±9.55[b]
	8	-7.87±0.19[a]		-11.59±0.17[a]		-15.89±0.12[a]		168.67±3.91[d]	

[a, b] : Values in the same column with different letters are significantly different (α=0.05)

The results of variance analysis for the ice crystallization temperatures (peak, onset and endset) showed that the type and level of biopolymer used were not statistically significant (P>0.05). However biopolymer type and level had a significant effect on the ice crystallization enthalpies of the samples (P<0.01). Addition of biopolymers caused a decrease in the enthalpy values compared to the control. On the other hand, lower enthalpy values were determined as the biopolymer level increased for all the samples (Table 1). The experimental DSC results of the melting process are shown in Table 2. It was observed that the melting temperatures (peak, onset and endset) and enthalpies of the samples were significantly affected by the biopolymer type and levels (P<0.01). As the biopolymer level increased, the lower temperatures and enthalpy values were detected for all the samples. Similarly, addition of biopolymers caused a decrease in the temperature and enthalpy values compared to the control and the lowest peak temperature values were obtained for the samples with xanthan gum.

The moisture contents (%) of the samples measured by TGA and the unfreezable water fractions (%) estimated based on DSC and TGA data are summarized in Table 3. In general, the unfreezable water is defined as the water that cannot be formed into ice even at very low temperatures [30, 31]. The level of unfreezable water fraction in the system is important for understanding the solid–liquid fraction composition at freezing temperatures [32]. The use of biopolymers and usage levels significantly affected the moisture contents and unfreezable water fractions of chicken meat samples (P<0.01). It was observed that biopolymer addition caused lower moisture contents and higher unfreezable water fractions in the samples. Also increased biopolymer levels decreased water contents. On the other hand 2% and 4% levels have similar values with the control for unfreezable water contents, which implies that the ratio of biopolymer in meat mixture has a significant effect on this parameter. This might be attributed to the hydration between the free water and the biopolymers, which made the water unfreezable.

Table 2. Effect of biopolymers on melting temperatures and enthalpies of chicken meat samples

Biopolymer	Ratio (%)	Temperature (°C)						Enthalpy (J/g)	
		Peak	Mean	Onset	Mean	Endset	Mean	ΔH	Mean
Control	-	-1.07±0.11^{a}	-1.07±0.11^{a}	-3.98±0.08^{a}	-3.98±0.08^{a}	1.49±0.12^{a}	1.49±0.12^{a}	194.85±1.43^{a}	194.85±1.43^{a}
	2	-1.15±0.17^{ab}		-4.28±0.22^{abc}		1.27±0.15^{ab}		186.58±5.54^{b}	
κ-Carrageenan	4	-1.27±0.09^{abc}	-1.29±0.17^{bc}	-4.31±0.25^{abc}	-4.24±0.21^{b}	1.18±0.23^{ab}	1.12±0.26^{bc}	181.39±0.39^{bc}	177.87±10.02^{b}
	8	-1.46±0.02^{cd}		-4.14±0.20^{ab}		0.91±0.29^{bc}		165.64±3.77^{d}	
	2	-1.28±0.05^{abc}		-4.50±0.05^{c}		1.35±0.16^{a}		185.40±4.21^{b}	
Xanthan gum	4	-1.35±0.13^{bc}	-1.43±0.20^{c}	-4.42±0.34^{bc}	-4.41±0.25^{b}	1.13±0.25^{ab}	1.01±0.41^{c}	176.14±2.48^{c}	173.16±12.95^{b}
	8	-1.66±0.15^{d}		-4.32±0.31^{abc}		0.56±0.31^{c}		157.93±7.79^{e}	
	2	-1.27±0.23^{abc}		-4.32±0.04^{abc}		1.36±0.16^{a}		187.75±2.89^{b}	
Gum arabic	4	-1.11±0.11^{ab}	-1.23±0.17^{b}	-4.39±0.04^{bc}	-4.23±0.19^{b}	1.34±0.20^{a}	1.30±0.25^{ab}	182.72±1.87^{bc}	178.06±11.43^{b}
	8	-1.32±0.12^{abc}		-3.98±0.05^{a}		1.20±0.39^{ab}		163.72±5.38^{de}	

$^{a, e}$: Values in the same column with different letters are significantly different (α=0.05)

Table 3. Effect of biopolymers on moisture contents and unfreezable water fractions of chicken meat samples

Biopolymer	Ratio (%)	Moisture content (%)	Mean (%)	Unfreezable water (%)	Mean (%)
Control		74.19±0.12^{a}	74.19±0.12^{a}	15.76±0.52^{c}	15.76±0.52^{b}
	2	71.68±2.15^{bc}		15.74±2.73^{c}	
κ-Carrageenan	4	71.14±0.33^{bc}	70.54±1.72^{b}	16.76±0.31^{bc}	17.21±2.10^{a}
	8	68.79±0.16^{de}		19.12±1.00^{a}	
	2	71.24±1.32^{bc}		15.64±0.55^{c}	
Xanthan gum	4	69.85±1.15^{cd}	69.36±2.41^{b}	17.04±1.21^{bc}	17.44±2.24^{a}
	8	66.99±2.49^{e}		19.64±2.45^{a}	
	2	72.42±0.14^{ab}		16.12±0.97^{c}	
Gum arabic	4	71.95±0.28^{b}	71.03±1.77^{b}	17.16±0.28^{bc}	17.63±1.92^{a}
	8	68.71±0.40^{de}		19.62±2.01^{a}	

$^{a, e}$: Values in the same column with different letters are significantly different (α=0.05)

These results revealed that addition of biopolymers to the chicken meat samples provides lower ice crystallization enthalpies, melting temperature and enthalpy values because of the decreased moisture contents and increased unfreezable water fractions. Also, it was reported that polysaccharides such as gums and carrageenan, are added to many frozen food formulations at low concentrations and are effective at stabilizing products against rapid ice crystal growth. During freezing, an unfrozen phase containing a high concentration of dissolved solutes is formed as water is separated from solution in the form of ice. This unfrozen phase is capable of undergoing a glass transition at low temperatures [33].

A glass transition is observed as an endothermic step change (i.e., baseline shift) in a DSC heat flow curve during heating [34]. Such an endothermic step change was observed in heat flow curves in the experiments and it was regarded as the glass transition (Figure 1). The temperature values (onset, endset and midpoint) obtained from the DSC curves about the glass transition are summarized in Table 4. T_g of the chicken breast meat was in the range of -17.83±0.02°C to -16.12±0.13°C and determined as -17.08±0.04°C (midpoint). Similar results were reported by Delgado and Sun [2] and Sunooj et al. [4] for chicken breast meat as -16.83°C and -16.63°C respectively. However, the addition of biopolymers and addition levels significantly affected the transition temperature values (onset, endset and midpoint) (P<0.01). The average higher T_g values (midpoint) were obtained for the samples with xanthan gum and κ-carrageenan as -15.99±0.42°C and -16.19±0.84°C respectively. Also the addition levels of biopolymers increased the T_g values for xanthan gum and κ-carrageenan and the higher T_g values were determined for the levels of 4% and %8 xanthan gum and %8 κ-carrageenan.

It was reported that T_g is an important factor for stabilization of frozen foods because it limits the diffusion of water within a frozen food [11]. Because it has recently become evident that the T_g of a food influences its shelf life, increasing the T_g leads to an important technology for extending this period [35]. Brake and Fennema [18] claimed that to achieve a glassy-state condition during commercial storage one could either lower the storage temperature, which may not be economically feasible, or increase T_g of the food by addition of biopolymers. They also stated that the latter approach would be feasible only for fabricated foods.

By adding biopolymers with high molecular weight to food systems, their glass transition temperature can be increased and they can therefore be stored at higher temperatures with greater stability and longer storage life with respect to diffusion-limited reactions [15, 35-37]. Levine and Slade [37] explain the cryoprotective effects of many high molecular weight biopolymers according to "cryostabilization" theory based upon the ability of high molecular weight solutes to reduce water mobility, thereby raising the T_g of a solution. Cryostabilization of food proteins would require addition of a high molecular solute to raise the T_g to a temperature above that of the storage temperature, thereby ensuring that the unfrozen liquid in the food system is in the glass state. This would theoretically halt (on a practical time scale) those deteriorative processes that are diffusion limited [38].

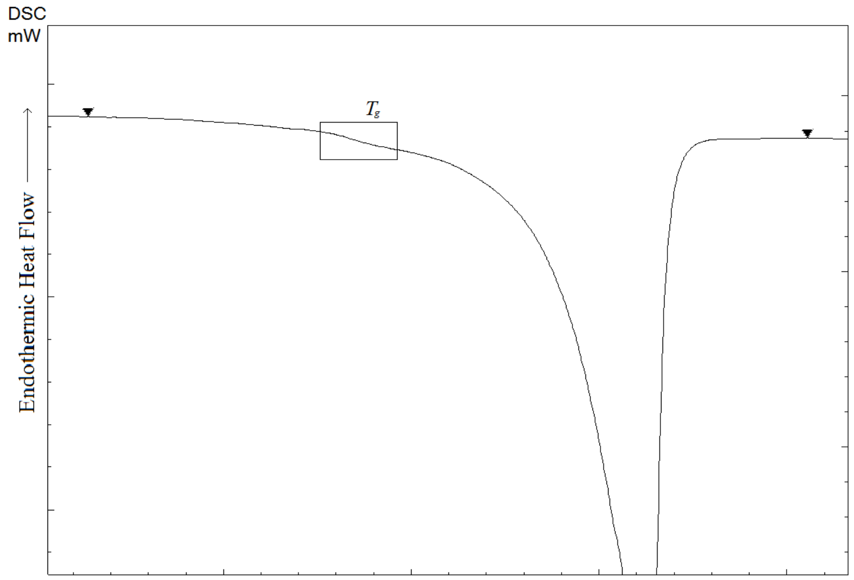

Figure 1. Representation of T_g region in DSC heat flow curve

Table 4. Effect of biopolymers on T_g values of chicken meat samples

Biopolymer	Ratio (%)	T_g (°C)					
		Onset	Mean	Endset	Mean	Midpoint	Mean
Control		-17.83±0.02[d]	-17.83±0.02[b]	-16.12±0.13[cde]	-16.12±0.13[b]	-17.08±0.04[b]	-17.08±0.04[b]
κ-Carrageenan	2	-17.76±0.12[cd]		-15.63±0.18[cd]		-16.69±0.16[b]	
	4	-17.76±0.26[cd]	-17.31±0.91[ab]	-15.44±0.14[bc]	-15.17±0.79[a]	-16.44±0.09[b]	-16.19±0.84[a]
	8	-16.42±1.18[a]		-14.45±1.12[a]		-15.45±1.22[a]	
Xanthan gum	2	-17.39±0.22[bcd]		-15.77±0.20[cde]		-16.52±0.17[b]	
	4	-16.49±0.13[a]	-16.86±0.52[a]	-14.79±0.14[ab]	-15.09±0.60[a]	-15.78±0.07[a]	-15.99±0.42[a]
	8	-16.71±0.57[ab]		-14.70±0.57[ab]		-15.69±0.23[a]	
Gum arabic	2	-18.10±0.13[d]		-16.20±0.23[cde]		-17.12±0.06[b]	
	4	-17.77±0.26[cd]	-17.62±0.59[b]	-16.39±0.32[de]	-16.37±0.41[b]	-16.99±0.20[b]	-16.93±0.23[b]
	8	-16.99±0.56[abc]		-16.51±0.68[e]		-16.68±0.09[b]	

[a, e] : Values in the same column with different letters are significantly different (α=0.05)

Auh et al. [39] detected that the T_g of a model solution containing bovine serum albumin increased as the average molecular weight of the added highly concentrated branched oligosaccharides increased. They also found that compared with the control, the amount of unfrozen water increased while decreasing its mobility, which reflected the preservation of proteins in rigid water-highly concentrated branched oligosaccharides structures. Kurozawa et al. [40] determined that the addition of maltodextrin or gum arabic increased the T_g of the chicken meat protein hydrolysate and, consequently, contributed to the stability of the powder. Mitsuiki et al. [41] observed that the T_g of carrageenan containing 24.5% water as 62°C by dynamic mechanical analysis. But, they concluded that the T_g values of agars and carrageenans would be reduced by the severing of inter- and intramolecular interactions, according to the quantity of water molecules interacting with their functional groups.
In some cases, the glass transition temperature was strongly influenced by the biopolymer. For example, Kasapis et al. [42] reported that the incorporation of 1% κ-carrageenan and 15mM potassium in 80-85% solids glucose syrup-sucrose increased the rheologically measured T_g from -25 to -1°C. Contrary to the reported increase of the rheologically determined glass transition temperature, Kumagai et al. [43] observed that in the presence of gelling agents, the addition of 0.9% carrageenan to glucose syrup with and without KCl, had no effect on the DSC measured T_g. In addition, there was no effect on molecular mobility in the glassy region. Also Brake and Fennema [18] found that the addition of 1% gelatin to minced mackerel resulted in no significant change in T_g and they concluded that the T_g of a fabricated food stored at a subfreezing temperature cannot be increased meaningfully by small amounts of added hydrocolloid. In this study, it was observed that T_g of the chicken meat samples were increased for addition level of %8 κ-carrageenan as well as 4% and 8% xanthan gum based on midpoint values.

CONCLUSIONS

The ice crystallization and melting temperatures and enthalpies as well as T_g values were determined for chicken breast meat with addition of different levels of xanthan gum, κ-carrageenan and gum arabic by using DSC. Biopolymer types and addition levels affected these values differently and the most effective biopolymer was observed as xanthan gum compared to others. Addition of high levels of κ-carrageenan and xanthan gum to the chicken breast meat significantly affected and increased the T_g value, which is regarded as an important factor to protect frozen foods from deteriorative reactions. These results are quite meaningful for the fabricated chicken meat products stored at subfreezing temperatures.

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