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

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 (Tg), 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 Tg (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 Tg 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 Tg values. Low molecular weight polymers and monomers in their pure form have a low Tg whereas longer chain molecules have higher Tg [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 Tg [14]. Thus the addition of any additive with high molecular weight in food can increase the Tg value. Addition of biopolymers to food systems could increase Tg, and they can therefore be stored at higher temperatures with greater stability and longer storage life [15].

There are several published values for Tg of beef and various fish species [16-26]. However there are only few studies about the Tg 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 Tg 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 (aw)

Water activity values of the samples were determined with a TH-500 aw 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 aw 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°C, ΔHm = 28.45 J/g), distilled water (mp = 0°C, ΔHm = 335 J/g) and heptane (mp = -91°C, ΔHm = 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 N2 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 60 min [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 follows:

\[ W_u = W_t - \left( \Delta H_f / \Delta H_w \right) \quad \text{(Eq. 1)} \]

where \( W_u \) is the unfreezable water mass fraction (%), \( W_t \) is the total water content (%), \( \Delta H_f \) and \( \Delta H_w \) 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.

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

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Ratio (%)</th>
<th>Temperature (°C)</th>
<th>Enthalpy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak</td>
<td>Mean</td>
<td>Onset</td>
</tr>
<tr>
<td>Control</td>
<td>-7.8(1.24)</td>
<td>-7.8(1.24)</td>
<td>-11.8(3.05)</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>4</td>
<td>-7.2(1.04)</td>
<td>-7.0(1.24)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-7.8(1.39)</td>
<td>-11.5(0.17)</td>
</tr>
<tr>
<td>Carrageenan</td>
<td>4</td>
<td>-8.4(1.86)</td>
<td>-7.6(1.12)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-7.4(4.60)</td>
<td>-8.7(1.74)</td>
</tr>
<tr>
<td>Gum arabic</td>
<td>4</td>
<td>-7.4(0.43)</td>
<td>-7.5(0.56)</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>-7.8(0.43)</td>
<td>-11.5(0.17)</td>
</tr>
</tbody>
</table>

*: Values in the same column with different letters are significantly different (α=0.05)

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 \( T_r \), may help to improve the shelf stability [4]. Studies indicated that the concept of \( T_r \) 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.

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

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Ratio (%)</th>
<th>Temperature (°C)</th>
<th>Enthalpy (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak</td>
<td>Mean</td>
</tr>
<tr>
<td>Control</td>
<td></td>
<td>-1.07±0.11</td>
<td>-1.07±0.11</td>
</tr>
<tr>
<td>κ-Carrageenan</td>
<td>2</td>
<td>1.15±0.17</td>
<td>-4.28±0.22</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.27±0.09</td>
<td>-4.31±0.25</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.46±0.02</td>
<td>-4.14±0.20</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>2</td>
<td>1.28±0.05</td>
<td>-4.50±0.05</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.35±0.13</td>
<td>-4.42±0.34</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.66±0.15</td>
<td>-4.32±0.11</td>
</tr>
<tr>
<td>Gum arabic</td>
<td>2</td>
<td>1.27±0.23</td>
<td>-4.32±0.04</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>1.11±0.11</td>
<td>-4.39±0.04</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1.32±0.12</td>
<td>-3.98±0.05</td>
</tr>
</tbody>
</table>

* a, b: 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

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Ratio (%)</th>
<th>Moisture content (%)</th>
<th>Mean (%)</th>
<th>Unfreezable water (%)</th>
<th>Mean (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>74.19±0.12</td>
<td>74.19±0.12</td>
<td>15.76±0.52</td>
<td>15.76±0.52</td>
</tr>
<tr>
<td>Control</td>
<td>2</td>
<td>71.68±2.15</td>
<td>71.14±0.33</td>
<td>16.76±0.31</td>
<td>17.21±2.10</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>68.79±0.16</td>
<td>69.54±1.72</td>
<td>19.12±1.00</td>
<td>19.64±1.00</td>
</tr>
<tr>
<td>κ-Carrageenan</td>
<td>2</td>
<td>71.24±1.32</td>
<td>69.85±1.15</td>
<td>15.64±0.55</td>
<td>15.64±0.55</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>69.85±1.15</td>
<td>69.36±2.41</td>
<td>17.04±1.21</td>
<td>17.44±2.24</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>66.99±2.49</td>
<td>66.99±2.49</td>
<td>19.64±2.45</td>
<td>19.64±2.45</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>2</td>
<td>72.42±0.14</td>
<td>71.95±0.28</td>
<td>16.12±0.97</td>
<td>16.73±1.92</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>71.95±0.28</td>
<td>71.03±1.77</td>
<td>17.16±0.28</td>
<td>17.16±0.28</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>68.71±0.40</td>
<td>71.03±1.77</td>
<td>19.62±2.01</td>
<td>19.62±2.01</td>
</tr>
</tbody>
</table>

* a, b: 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 associated with the glass transition are summarized in Table 4. \( \Delta T_g \) of the chicken breast meat was measured in Table 4. \( \Delta T_g \) of the chicken breast meat was determined in the range of -17.83±0.02°C to 16.12±0.13°C and in the range of -15.99±0.42°C and -16.19±0.84°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 \( \Delta T_g \) 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 \( \Delta T_g \) values for xanthan gum and κ-carrageenan and the higher \( \Delta T_g \) values were determined for the levels of 4% and %8 xanthan gum and %8 κ-carrageenan.

It was reported that \( \Delta T_g \) 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 \( \Delta T_g \) of a food influences its shelf life, increasing the \( \Delta T_g \) 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 \( \Delta T_g \) 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 \( \Delta T_g \) of a solution. Cryostabilization of food proteins would require addition of a high molecular solute to raise the \( \Delta T_g \) 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].
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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

![Figure 1. Representation of $T_g$ region in DSC heat flow curve](image)

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

<table>
<thead>
<tr>
<th>Biopolymer</th>
<th>Ratio (%)</th>
<th>Onset (°C)</th>
<th>Mean (°C)</th>
<th>Endset (°C)</th>
<th>Mean (°C)</th>
<th>Midpoint (°C)</th>
<th>Mean (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>2</td>
<td>-17.83±0.02</td>
<td>-17.83±0.02</td>
<td>-16.12±0.13</td>
<td>-16.12±0.13</td>
<td>-17.08±0.04</td>
<td>-17.08±0.04</td>
</tr>
<tr>
<td>κ-Carrageenan</td>
<td>4</td>
<td>-17.76±0.12</td>
<td>-17.31±0.91</td>
<td>-15.44±0.14</td>
<td>-15.17±0.79</td>
<td>-16.44±0.09</td>
<td>-16.19±0.84</td>
</tr>
<tr>
<td>Xanthan gum</td>
<td>2</td>
<td>-17.39±0.22</td>
<td>-16.86±0.52</td>
<td>-14.70±0.57</td>
<td>-15.09±0.60</td>
<td>-15.78±0.07</td>
<td>-15.99±0.42</td>
</tr>
<tr>
<td>Gum arabic</td>
<td>2</td>
<td>-18.10±0.13</td>
<td>-17.62±0.59</td>
<td>-16.20±0.23</td>
<td>-16.37±0.41</td>
<td>-16.99±0.20</td>
<td>-16.93±0.23</td>
</tr>
</tbody>
</table>

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


