Biblid: 1821-4487 (2014) 18; 3; p 100-102
UDK: 542.934.8:641.12

Original Scientific Paper
Originalni naučni rad

THE GLASS TRANSITION OF OSMOTICALLY DEHYDRATED PORK MEAT

STAKLASTI PRELAZ OSMOTSKI DEHIDRIRANOG SVINJSKOG MESA

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ABSTRACT

Thermal behavior of and fresh and osmotically dehydrated pork meat in sugar beat molasses pork meat was studied by Differential scanning calorimetry (DSC). Samples of 7–11 mg (moisture content 5-20%) of osmotically dehydrated pork meat in aluminum pans were cooled from 20°C to −90 °C, equilibrated for 5 min and scanned initially from −90 °C to 150 °C at a rate of 5°C/min. The glass transition temperature (T_g) was determined from the DSC heat flow curves with TA Advantage software. Since much of the water was bound to the solid matrix, samples with low moisture content only showed up the glass transition. T_g decrease with increasing moisture content. T_g decreased from −6.0 °C to −10.1 °C when the moisture content increased from 5% to 20%. DSC curves of fresh pork meat did not showed the glass transition.

Key words: *pork meat, osmotic dehydration, glass transition, differential scanning calorimetry.*

REZIME

Termalne karakteristike svežeg i osmotski dehidriranog svinjskog mesa u melasi šećerne repe, praćene su metodom diferencijalne skenirajuće kalorimetrije (DSC). Uzorci osmotski dehidriranog svinjskog mesa, mase od 7–11 mg (sadržaj vlage 5-20%) hlađeni su od 20°C do −90 °C, uravnoteženi 5 min a zatim grejani od −90 °C do 150 °C brzinom grejanja 5°C/min. Temperatura staklastog prelaza (T_g) određena je iz dobijene DSC krive pomoću programa TA Advantage. Kod uzoraka s malim procentom vlage, nađen je staklasti prelaz, pošto je veliki udeo vode vezan za čvrsti matriks. Povećavanjem sadržaja vlage u uzorku (5-20%) snižavaju se temperature staklastog prelaza od −6,8 °C do −10,3 °C. Rezultati DSC analize svežeg mesa pokazali su izostanak staklastog prelaza.

Ključne reči: *svinjsko meso, osmotska dehidratacija, staklasti prelaz, diferencijalna skenirajuća kalorimetrija.*

INTRODUCTION

The importance of T_g of amorphous food materials for processing and storage stability has been recognized and emphasized by many researchers and a wide range of potential food applications of the glass transition phenomenon have been identified (*Shia et al., 2009*). Water activity (a_w) and glass transition temperature (T_g) provide valuable information on the effects of water content on water availability in foods and on the physical state of food solids (*Roos, 1995*). Water activity, which is defined by the chemical potential of water, measures the availability of water for deteriorative changes or microbial growth. Glass transition is a second-order phase transition, a property of the food matrix that occurs over a characteristic glass transition temperature range (*Roos, 2003*), and it is a highly important characteristic in understanding many aspects of food stability and processing. For many decades, the concept of a_w has been sufficient to describe the stability of food products. It has been argued that a_w is not sufficient to describe the secondary processes of change-in-state in foodstuffs thus ushering in the concept of glass transition temperature (*Slade and Levine, 1991*). Over the last two decades, much research has been reported on the importance of glass transition for a large variety of food materials and ingredients. As a_w was proved to be inadequate in some cases, the concept of glass transition was used as a parameter for quantifying water mobility and food stability, which became popular in the late 1980s (*Oliveira et al., 1999*). Biological materials are rigid and brittle below the glass transition temperature. Nevertheless, they are not crystalline with regular structure but retain the disorder of the liquid or amorphous state (*Rahman et al., 2003*). The physical state of foodstuffs is very stable below the glass transition temperature because compounds involved in deterioration reactions take many months or even years to diffuse over molecular distances, and approach each other to react (*Slade and Levine, 1991*). Furthermore, water molecules become kinetically immobilized within the concentrated phase, thus being unable to support or participate in the reactions causing deterioration (*Mitchell, 1998*). Most scientists concur that the glass transition temperature under conditions of maximal freeze concentration, T_g, is the technologically significant transition which has the greatest influence on low-temperature stability (*Goff, 1994*). The consequence as far as food products are concerned is that a small change in temperature in the vicinity of the glass transition temperature will result in pronounced changes in the sensory properties of texture and other dynamic properties (*Simatos et al., 1995, Delgado and Sun, 2002*). Glassy and freezing characteristics of pure substances are more commonly reported than that of real foods, which are complex multicomponent mixtures (*Rahman et al., 2003*). The glass transition temperatures of freezedried strawberry and cabbage are available and were measured as a function of water content by Roos (*Roos, 1995*) and Paakkonen and Plit (*Paakkonen and Plit, 1991*), respectively, using differential scanning calorimetry (DSC). *Brake and Fennema, 1999* and *Inoue and Ishikawa, 1997* also measured the glass transition of fresh muscle tissue by DSC. *Brake and Fennema, 1999* pointed out on the importance of the annealing for T_g, determination, and found that apparent T_g, of mackerel, cod and beef were similar (ca -11 to -13ºC) and substantially higher than most published values (-15 ºC to -77 ºC for tuna and beef). *Inoue and Ishikawa, 1997* found that glass transition of fresh red meat of bigeye tuna (*Thunnnas obesus*) and its filtrate occurred between -71ºC and -68 ºC, independent of cooling rate from 1 K/min up to 50 K/min. Also the same authors showed that the transition at low temperature appeared to occur in the liquid part and neither dilution nor concentration of the filtrate affected the glass transition temperature (T_g) but the solute concentration of the freeze concentrated phase (Cg) was affected.

The objective of the present study was to define thermal behavior of fresh and osmotically dehydrated pork meat considering glass transition.

MATERIAL AND METHOD

Preparation of osmoticaly dehydrated pork meat (*Musculus brachii*) in sugar beat molasses has been described elsewhere (*Šuput et al., 2013, Pezo et al., 2013*). A differential scanning calorimeter (DSC, Q1000, TA Instruments, New Castle, DE) equipped with Refrigerated Cooling System (RCS, TA Instruments, New Castle, DE), was used to perform DSC experiments. The calorimeter was calibrated according to the instruction provided by TA instruments user manual by checking temperature and enthalpy of fusion of indium as standard. Osmoticaly dehydrated pork meat samples (7–11 mg) with different water content, were placed in aluminum pans and subjected to cooling and heating, in the temperature range from -90 ºC to 150 ºC, with controled heating rate Hr=5 ºC/min, under the N_2 purge flow of 50 ml/min.

First, samples were cooled to −90 ºC and equilibrated for 5 min and then scanned from −90 ºC to 150 ºC at a heating rate of 5ºC/min. The wather content was estimated by Thermoogravimetric analysis (TGA). TGA measurements were performed on TGA Q 500, (TA Instruments, New Castle, DE) under N_2 purge flow of 60 ml/min and 40 ml/min, in sample and balance, respectively. All TGA scans were performed in temperature range 25 ºC-900 ºC, and heating rate Hr= 5 ºC/min.

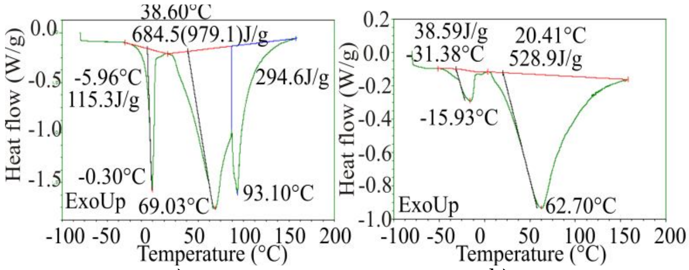
Each thermogram was analyzed by TA Advantage Universal analysis 2000 software to obtain the glass transition parameters (onset, T_{onset}; midpoint, T_g; final ,T_{end}) for the onset, mid and end of transition, and also to obtain the percentage of mass loss from TGA curves.

Three replicates were used for selected samples (water content). For the materials showing wide peak of ice melting on the DSC thermogram, the point of maximum slope corresponds well with the initial freezing point estimated from cooling curve method (*Sablani et al., 2007*). The enthalpy of ice melting was estimated from the area of the melting endotherm. The average values and standard deviation of three replicates were obtained for selected data point to identify the experimental variability.

The water activity (a_w) has been determined by thermoanalytical techniques as previously described by *de Silva et al. 2008).*

RESULTS AND DISCUSSION

Thermal behavior of pork meat samples are shown in *Figures 1.a), b)* and *2*. For fresh pork meat (moisture content 75%), the heat flow curve obtained from DSC showed three characteristic transitions (Fig.1. a) with peak maximums at about -0.3 ºC, 69 ºC and 93 ºC which represents ice melting, water evaporation and meat protein denaturation with total enthalpy of 970 J/g, respectively. First transition, at -0.3°C, corresponds to the ice melting, second transition, which occurs at 69ºC, was assigned to collagen (*Stabursvik and Martens, 1982*) and the third transition has been assigned to actin denaturation (*Stabursvik and Martens, 1980*). In Fig. 1. b) DSC curve of osmotically dehydrated pork meat (moisture content 38.1%) is presented. For osmotically dehydrated pork meat the heat flow curve obtained from DSC showed two characteristic endothermal transitions (Fig.1. b). The first one, with peak maximum at -16 ºC represents ice melting and second one, corresponds to the process of protein denturation which is accompanied with water evaporation, and presented as one broad endothermal peak with temperature maximum T_m=63 ºC and total enthalpy (ΔH) of 529 J/g. Decreased enthalpy and temperature maximum of transition which represents meat protein denaturation of osmoticaly dehydrated pork meat (second transition) compared to for fresh pork meat (second transition) suggest that destabilization of meat proteins and conformational changes were induced by the process of osmotic dehydration. These changes of material thermal behavior were consequence of water loss and interaction with molasses components. This is a typical DSC thermogram of sample having freezeable water without annealing (Fig. 1. b), in accordance with literature (*Shia et al., 2009*). It showed ice melting point (-31.4 ºC), with total enthalpy of trasition ΔH=38.6 J/g .



a) b)

Fig. 1. Typical DSC curve of a) fresh pork meat and b) osmotically dehydrated pork meat

Further loss of water leads to new changes in the material and the appearance of characteristic thermal behavior for samples having unfreezible water (*Shia et al., 2009, Sablani et al., 2007, Delgado and Sun, 2002, Rahman et al., 2003*). Since much of the water was bound to the solid matrix, samples of dehydrated pork meat with low moisture content (below 20%) only showed up the glass transition. As expected T_g decreased with increasing moisture content, as shown in Table 1.

Table 1. Water content, glass transition temperature, freezing point and water activity of osmoticaly dehydratated pork meat with freezable and unfreezible water

Moisture (%)	T_{onset} (ºC)	T_g (ºC)	T_{end} (ºC)	Ice melting (ºC)	a_w
38.10	-	-	-	-37.4±1.0	0.745
35.02	-	-	-	-33.4±0.9	0.732
26.28	-	-	-	-33.7±0.8	0.724
20.70	-	-	-	-31.6±1.1	0.720
5.90	-20.2±3.0	-10.3±1.1	-2.62±2.5	-	<0.7*
3.77	-17.2±3.1	-6.8±1.0	-1.81±2.7	-	<0.7*

Cannot be determined by thermoanalytical techniques in samples having unfreezible water.

T_g decreased from −6.8 ºC to −10.3 ºC when the moisture content increased from 4 to 20 % (*Table 1*).

For pork meat with water content from 20% to 4% the heat flow curves obtained from DSC showed up the characteristic glass transition (Fig. 2).

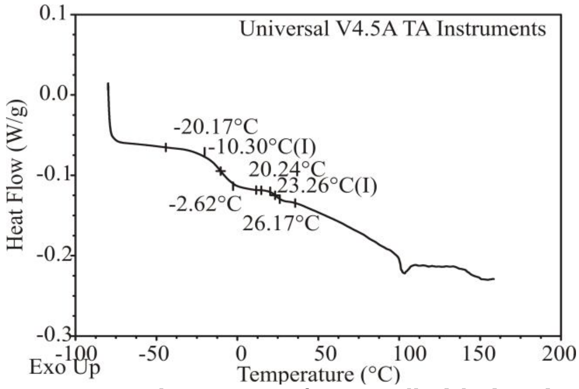


Figure 2. Typical DSC curve of osmotically dehydrated pork meat with low moisture content (<20%)

A decrease in heat flow caused by a glass phase transition was observed in the thermogram in temperature region from -5 ºC to – 25 ºC, and disappearance of endothermic peaks between -30 ºC to 150 ºC, usual for samples having freezable water, occurred (Fig. 1.b and Fig. 2). The glass phase transition was found consistently in samples of different a_w and water content (*Shia et al., 2009, Kawai et al., 2005*). It was reported that two kinds of glass transitions have been observed with protein–water systems. One is known to be at low temperatures (around −113 ºC to −73 ºC) which are associated with freezing of motions of water molecules (*Sablani et al., 2007*). However, the transition observed in this work was at a relatively higher temperature which could be due to the initiation of mobility in protein molecules what is agreeable to literature (*Sablani et al., 2007, Shia et al., 2009*). It can be assumed that initiation of protein molecules mobility could be induced not only by water loss but also with protein interaction to molasses components. On the other hand, results obtained in this work are in agreement with results obtained by *Brake and Fennema 1999*, who found that apparent T_g of mackerel, cod and beef were similar (-11 ºC to -13 ºC) and substantially higher than most published values (-15 ºC to -77 ºC for tuna and beef), but in accordance with expectations for substances of high molecular weight. Samples with higher water content (from 26 to 38 %) did not have glass transition in studied temperature range. In the Table 1 are also given the ice melting point temperatures as a function of moisture content. The results showed that ice melting increased with increasing of solid content.

CONCLUSION

The samples of osmotically dehydrated pork meat with different moisture percentage and a_w value behaved differently during DSC scanning. Since much of the water was linked to the solid matrix, samples with low moisture content (under 20%) only showed up the glass transition. As expected T_g decreased with increasing moisture content: T_g decreased from −6.8 ºC to −10.3ºC when the moisture content increased from 4 to 20%. DSC curves of fresh pork meat did not showed the glass transition under scanning conditions applied in this work.

Glass transition temperatures T_g observed in this work was at a relatively higher temperature but still agreeable to literature (*Sablani et al., 2007, Shia et al., 2009, Brake and Fennema, 1999).* It can be proposed that initiation of protein molecules mobility could be induced not only by water loss but also with protein interaction to molasses components. Further studious investigations are necessary. Obtained data of sample thermal behavior can be useful in the construction of a state diagram for osmotically dehydrated pork meat.

ACKNOWLEDGMENT:This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, under the Projects No TR-31055 and TR-31093.

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Received: 28. 02. 2014. Accepted: 28. 03. 2014.