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# On the Thermal Properties of Frozen, Refrozen and Freeze Drying Porcine *Longissimus dorsi*

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**Abstract:** Modulated Differential Scanning Calorimetry (Modulated DSC) was used to investigate the protein denaturation characteristics of *Longissimus dorsi* muscle at different conditions; fresh, frozen and refrozen. Meat was also freeze drying to determinate its thermal properties. The thermograms indicated three exothermic peaks between 45-85°C, corresponding to denaturation of myosin (peak 1), sarcoplasmic proteins (peak 2) and actin (peak 3). Refrozen process significantly affected denaturation enthalpy reducing the value from 2.69-2.21 J $g^{-1}$. Samples submitted to freeze drying showed a single sharp peak centered about 81.85°C with a similar trend in regards to denaturation enthalpy. In the case of heat Capacity (Cp), the maximum change was observed at 80°C with a reduction following the order; fresh, frozen and refrozen. This phenomenon was also found for freeze drying samples however, the single broad change was in the temperature range of 40-100°C. From these results, it is concluded that moisture content plays an important role in the thermal properties of meat.

**Key words:** Pork loin, modulated DSC, protein denaturation, enthalpy, heat capacity

## INTRODUCTION

Freezing is an important process in the meat industry; this preservation method protects the product from microbiological contamination, decreases the rates of some degradation reactions as well as modified ionic strength among others (Mortensen *et al*., 2006). Parameters such as freezing rate, meat fiber orientation, frozen temperature and time have strong influence in the final meat quality due to the formation and growth of ice crystals. The recommended temperature for meat freezing preservation is about -28°C (Ngapo *et al*., 1999) however, temperature variations during transportation or even storage can cause changes in the final product due to thawing and continuous water recrystalization, a common uncontrolled condition in the meat industry affecting the quality of the meat products.

It is well known that the combination of frozen and refrozen processes increases the original ice crystal size in about 20 times (Bevilacqua and Zaritzky, 1982) thus, producing cellular damage and alteration of meat properties such as texture, color and water retention capacity (Bevilacqua and Zaritzky, 1980; Do *et al*., 2004; Bertram *et al*., 2007; Sawyer *et al*., 2007). Changes in meat quality characteristics also have a relationship with the physicochemical and thermodynamic behavior. Differential Scanning Calorimetry (DSC) is a technique that can be used to elucidate the effect of the freezing process on certain thermal parameters of foods. In relation with the before mentioned, some researchers have studied thermal denaturation of muscle proteins (Stabursvik and Martens, 1980), water-protein interactions of porcine *Longissimus dorsi* (Christensen *et al*., 2011) as well as apparent specific heat of chicken breast patties using DSC (Murphy *et al*., 1998). However, Modulated DSC (MDSC) offers more reliability information in the characterization of food systems compared to conventional DSC since, it has a combination of excellent sensitivity and high resolution, providing more accurate results for weak and/or broad transitions.

Information in the literature is generally arrived for fresh meat and not for frozen, refrozen and freeze drying

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meat pork; consequently, the aim of this research was to study the effect of these processes over the thermal properties (transition temperatures, heat capacity and enthalpy) of porcine *Longissimus dorsi*.

## MATERIALS AND METHODS

**Raw material:** M. *Longissimus dorsi* were excised 48 h post mortem from both sides of three healthy castrated male porks of about 6 months of age (slaughter weight 110 kg aprox.). pH was measured (Hanna instruments, Model HI 99163, Romania) and used as a selection criteria for the muscles (pH 5.43±0.21). After selection, the muscles were stored at 4°C. Proximate composition was also determined for fresh meat (water content 75.30±1.19%, protein 21.83±2.54%, fat 1.87±0.09% and ash 1.0±0.03%) as confirmed using the corresponding AOAC (2002) methods. Determinations were done in triplicate.

**Freezing process:** Samples of approximately 50 g (1×12×10 cm) were cut from each muscle (n = 5) and frozen at -25°C using an Armfield FT36 air blast freezer (USA) with an average air flow rate of 3 m $sec^{-1}$. Three conditions were assayed: not frozen used as a control (fresh meat); frozen and refrozen meat. All conditions were also evaluated in a freeze drying state. Briefly, sub-samples of about 1 $cm^3$ were prefrozen at -70°C in a Revco ULT 39125H05 ultra-low temperature freezer (Asheville, NC, USA) for 24 h before freeze drying then freeze dried in an Labconco freeze drier (MO, USA) at a condenser temperature August 9, 2011 of -40±2°C and a pressure >0.10 mm Hg.

**Modulated DSC measurements:** Samples were analyzed using a differential scanning calorimeter equipped with a modulation extension apparatus (DSC 2920, TA Instruments, New Castle, USA). Cooling was carried out with a refrigerated cooling system (TA Instruments, New Castle, USA). The temperature calibration was performed using TA instruments software with indium (melting point value of 156.6°C, standard TA instruments, New Castle, USA). The heat capacity was calibrated with sapphire (aluminum oxide). The TA instruments universal analysis software was used to record and analyze the thermograms. Samples (24 mg for fresh meat and 8.5 mg for freeze drying meat) were packed down in hermetic aluminum DSC pans (TA Instruments, New Castle, USA). The DSC was operated in modulation mode. Samples were analyzed in triplicate by heating in the modulated DSC furnace in atmosphere of nitrogen at a rate of 10°C $min^{-1}$ with temperature modulation of 0.8°C 60 $sec^{-1}$. Thermal decomposition data for the samples were collected over the temperature range 30-120°C.

**Statistical analysis:** Data were assessed by Analysis of Variance (ANOVA) and means were separated by the Tukey procedure using the Statistical Analysis System (SAS, 1998). A significance value of ($\alpha$ = 0.05) was used to distinguish significant differences between treatments.

## RESULTS AND DISCUSSION

**Chemical proximate analysis and pH:** The results for the chemical composition and pH value for the fresh porcine muscle (*Longissimus dorsi*) are in close agreement with values reported previously (Chiavaro *et al*., 2009). The results indicated that the muscle has high moisture content (75.30%); enough water to promote ice crystal formation during freezing.

**Thermal analysis (total heat flow):** The modulated DSC thermograms of the fresh, frozen and refrozen meat as well as for the freeze drying samples are shown in Fig. 1. The thermograms indicated three exothermic peaks between 45-85°C for fresh, frozen and refrozen meat. Table 1 shows the denaturation temperatures and the enthalpy ($\Delta H_{total}$) for these samples.

Fresh meat exhibited the three main regions: myosin (about 56°C), myosin plus sarcoplasmic proteins and collagen (about 66°C) and actin (about 78°C) which compared well with the findings in the literature (Deng *et al*., 2002; Zhu *et al*., 2004). Total denaturation enthalpy of the fresh meat was 2.69 J $g^{-1}$; these results are in close agreement with values reported by Kazemi *et al*. (2009) who reported total denaturation enthalpy of 2.83 J $g^{-1}$ for pale, soft and exudative pork muscle. Frozen meat (-25°C) exhibited a denaturation enthalpy of

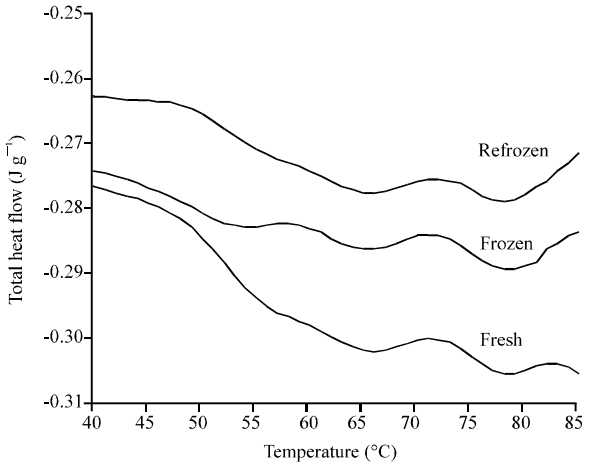


Fig. 1: Modulated DSC thermograms of *Longissimus dorsi* muscle; fresh, frozen and refrozen

Table 1: Denaturation temperatures ($T_d$) and enthalpy ($\Delta H_{total}$) of porcine *Longissimus dorsi*

| | Peak (°C) | | | |
|---|---|---|---|---|
| Meat samples | 1 | 2 | 3 | Enthalpy ($\Delta H_{total}$) (J $g^{-1}$) |
| Fresh | 57.55±0.01[a] | 66.09±0.01[a] | 78.72±0.07[a] | 2.69±0.03[a] |
| Frozen | 54.12±0.01[b] | 65.11±0.01[a] | 77.85±0.03[a] | 2.50±0.05[a] |
| Refrozen | 57.19±0.07[a] | 66.07±0.01[a] | 78.24±0.01[a] | 2.21±0.15[b] |

Mean of three replicates±standard error; Mean values with same letter in the same column are not significantly different (Tukey>0.05)

Table 2: Denaturation temperature ($T_d$) and enthalpy ($\Delta H_{total}$) of freeze drying porcine *Longissimus dorsi*

| Meat samples | Peak (°C) | Enthalpy ($\Delta H_{total}$) (J $g^{-1}$) |
|---|---|---|
| Fresh | 81.99±0.09[a] | 70.42±2.6[a] |
| Frozen | 81.83±0.10[a] | 64.39±3.1[b] |
| Refrozen | 81.76±0.13[a] | 57.13±2.1[c] |

Mean of three replicates±standard error; Mean values with same letter in the same column are not significantly different (Tukey>0.05)

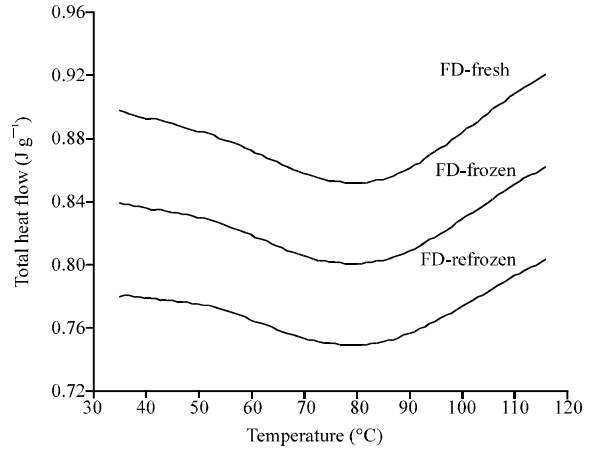


Fig. 2: Modulated DSC thermograms of freeze drying *Longissimus dorsi* muscle

2.50 J $g^{-1}$, only slightly different from the value for fresh meat. On the contrary, refrozen process induced additional protein denaturation reducing enthalpy to 2.21 J $g^{-1}$ (Table 1). The lack of differences in the modulated DSC profiles of fresh, frozen and refrozen samples suggests that the freezing process cause moderate protein denaturation, reducing denaturation enthalpy as shown in Table 1. Fernandez-Martin *et al.* (2000) also reported reduction in denaturation enthalpy for pork and beef muscles subjected to high-pressure-shift freezing. On the contrary, Mietsch *et al.* (1994) used SDS-PAGE to investigate proteins denaturation of pork samples stored at -20°C for up to 6 months. No significant changes in the electrophoretograms were observed during the entire period of frozen storage. These results suggest that another factor may have been responsible for the changes observed in denaturation profiles.

On the other hand, Fig. 2 shows modulated DSC thermograms for freeze drying samples. Under this condition, a single sharp peak centered about 81.85°C was

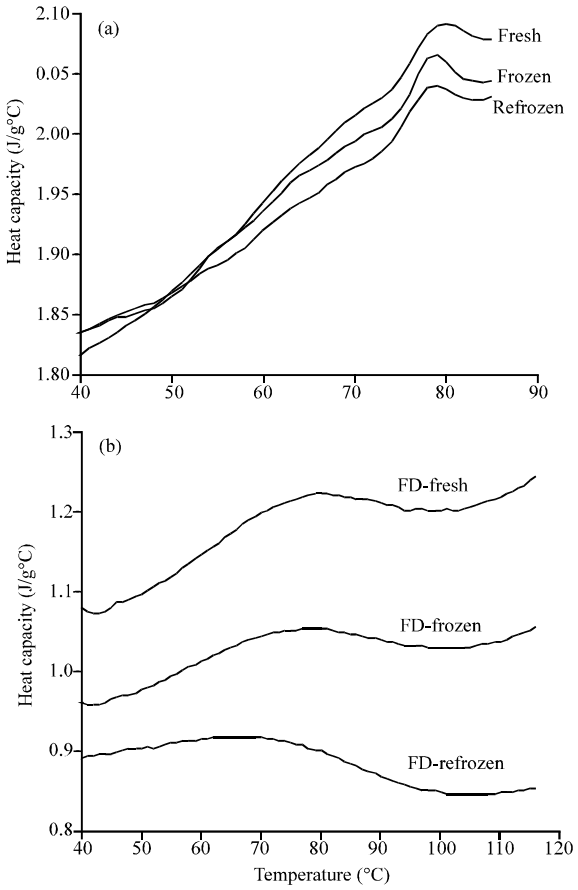


Fig. 3: Heat capacities of *Longissimus dorsi* muscle: a) fresh, frozen and refrozen meat; b) freeze drying samples

observed. Freeze drying treatment caused considerable protein denaturation; exotherm for myosin and myosin plus sarcoplasmic and collagen practically disappeared in these samples. Consequently, statistical differences in the $\Delta H_{total}$ were registered (Table 2). Fresh meat presented the highest denaturation enthalpy value (70.42 J $g^{-1}$) while refrozen meat showed the lowest denaturation enthalpy (57.13 J $g^{-1}$). In general, water content considerably influence de shape and size of the modulated DSC curves.

**Heat capacity**: Structural changes in foods are also estimated by means of the heat Capacity (Cp). Figure 3 shows the behavior of the Cp; continuous changes were

observed in the range of 45-85°C with a maximum change of about 80°C for fresh, frozen and refrozen samples (profile A). These samples presented similar curves however, a reduction in the Cp value was observed following the order; fresh, frozen and refrozen meat. Fresh meat presented the highest Cp value (2.09 J/g °C); the apparent heat capacity of these samples is similar to those reported by Kemp *et al.* (2009) who found Cp values between 1.5-2.7 J/g °C for pork (myofibrillar proteins) in the temperature range of 30-85°C. It is well known that thermal properties depend strongly on temperature and composition of the product (Sweat, 1995). On the other hand, frozen and refrozen meat samples presented Cp values of 2.07 and 2.04 J/g °C, respectively (Fig. 3a). This behavior could be possible related to the differences in moisture content since, water contributes in great extent to the apparent heat capacity. Figure 3b shows the heat capacity for freeze drying meat. In this case, all samples exhibited a broad change in the range of 40-100°C. Freeze drying fresh meat presented an average Cp value of 1.23 J/g °C while frozen and refrozen freeze drying samples presented values of 1.02 and 0.93 J/g °C, respectively. Very little is known about the Cp in freeze drying pork loins thus, the observations made in this research have not been conclusive. Consequently, more research on the effect of moisture content on other thermal properties of *Longissimus dorsi* muscle needs to be conducted.

## CONCLUSION

The measurements reported in this research extent the range of available thermal data of *Longissimus dorsi* muscle, specifically denaturation temperatures/enthalpy and heat capacity. Estimations were also conducted on freeze drying pork loin samples. Moreover, further studies are needed to obtain a better understanding on the behavior of the proteins subjected to frozen conditions.

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