Journal of Food Engineering 128 (2014) 111–118

Contents lists available at ScienceDirect

Journal of Food Engineering

journal homepage: www.elsevier.com/locate/jfoodeng

Thermal phase transitions and mechanical characterization of Atlantic cod muscles at low and ultra-low temperatures

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ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form 11 December 2013
Accepted 20 December 2013
Available online 31 December 2013

Keywords:
State diagram
Glass transition
Young's modulus
DSC

ABSTRACT

The glass transition of fresh cod were detected in the temperature range between −69.6 (1.5) and −84.2 (1.3) °C. The unfreezable moisture content was 5.1 (0.2)% wet basis (w.b.). The onset of ice melting was at −33.5 (0.6) °C. The state diagram was obtained as a consequence of using the Gordon–Taylor and modified Clausius–Clapeyron equations. The maximal freeze concentration was measured at 75.6% solids.

The rupture stress and Young's modulus increased linearly with the decreasing of temperature; their abrupt changes were observed between −80.0 and −85.0 °C, when both values increased sharply and then were stable until −130.0 °C. The rheological properties correlated with the thermal phase transition in the cod's tissues, and with the water state in the product. The abrupt changes in rapture strength and Young's modulus were related to the low temperature glass transition. The cod tissues in the glassy state showed only brittle properties.

1. Introduction

A fast freezing is considered to be the preferable way of fish processing, due to the formation of small intra- and extracellular ice crystals, which cause less damage to the fish tissues than larger crystals do. The application of a low ambient temperature for fish freezing is beneficial for the rapid freezing of seasonal or aquaculture species due to the increasing of a heat exchange. The ambient freezing temperatures can be decreased below −60.0 °C for blast freezers; alternatively, liquid nitrogen can be applied as an expensive but effective solution for valuable species. A better understanding of the thermal transitions in fish at such temperatures is required for making the fast freezing process more effective.

Along with the advantages of fast freezing, several negative effects have also been observed. A sharp decreasing of the temperature during freezing leads to a fracture deformation of the food's tissues, which results in cracks (Shi et al., 1999). In the case of fish, it also leads to the separation of meat from a back-bone and to the breakage of miomers. For example, portions of salmon frozen in liquid nitrogen contained numerous small intracellular ice crystals while those which had been air frozen at −20.0, −40.0 and −80.0 °C contained less. At the same time, a large amount of cracks were observed in the samples frozen in liquid nitrogen (Ottestad et al., 2011). Thus, a balance between the rate of freezing and the structural changes should be maintained.

Several models explain the strain–stress dependence during the freezing of food with some limitations, and assume that only first order phase transitions take place in the food during freezing (McKellar et al., 2009; Pham et al., 2006; Shi et al., 1999). At the same time, several second order transitions can be detected in the food products (Rahman, 2006). The glass transition of food is characterized by a sharp increase of Young's modulus and changing of the rheological properties of food from ductile to brittle (Champion et al., 2000). This event can be responsible for the structural damage of the product during the rapid freezing and the frozen storage.

The glass transition in fish muscles appears at ultra-low temperatures in the range between −83.1 and −52.2 °C (Orlien et al., 2002; Rahman et al., 2003; Shi et al., 2009) and higher temperatures in the range between −21.0 and −11.0 °C (Brake and Fennema, 1999; Nedenskov Jensen et al., 2003). The rheological properties of the fish tissues have not been studied at these temperature ranges.

The scope of this article is to investigate the Young's modulus, fracture stress, and rupture point of cod muscles, with respect to the thermal transitions at freezing temperatures. The information obtained is essential for the prediction of the freezing process, when ultra-low temperatures are applied.

2. Materials and methods

2.1. Sample preparation

The farmed Atlantic cod (*Gadus morhua*) fillets (Leroy, Norway) were stored on ice for 24 h. A middle part of the back side of the

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http://dx.doi.org/10.1016/j.jfoodeng.2013.12.025

Nomenclature

B	ratio of unfreezable water to the total solids content, kg kg^{-1}
DSC	differential scanning calorimeter/calorimetry
E	melting energy, kJ
I	mass of ice, kg
L	latent heat, kJ kg^{-1}
M	molecular mass, kg mol^{-1}
R	molecular mass ratio of water and solids, kDA kDa^{-1}
T	temperature, °C
Y	Young's modulus, MPa
k	system's constant in Gordon–Taylor equation
w.b.	wet basis
x	mass fraction kg kg^{-1}

Greek symbols

β	molar freezing point constant, 1860 kg K kg^{-1} mol^{-1}
δ	depression of freezing point, °C
ε	strain, %
σ	stress, MPa

Subscripts

ge	end point of glass transition
gi	inflection point of glass transition
go	onset point of glass transition
f	freezing
m	melting
om	onset of ice melting
s	solids
w	water

fillets (thickness between 0.03 and 0.04 m) was used for all the types of experiments presented in this article.

For the compressive stress experiment the samples were prepared in the following order. A part of the fish muscles with the dimensions 0.03 × 0.04 × 0.10 m was frozen in a laboratory freezer at −10.0 ± 1.0 °C until the consistency became good enough to cut it precisely into smaller samples with the dimensions 0.01 × 0.01 × 0.02 m. These samples had miomers running horizontally one by one. Then the samples were equilibrated in a laboratory freezer for 2 days at the following temperatures: −20.0, −30.0, −36.0, −50.0,−75.0, −80.0, and −85.0 °C. Temperature deviation did not exceed ±1.0 °C.

Fresh and dried samples were used in the DSC study. Fresh samples were obtained directly from the fillets with a lancet to avoid the connective tissues. Dried samples were obtained by the following procedure. For freeze drying, an Alpha 2–4 LSC Plus vacuum-freeze dryer, equipped with a LyoCube 4–8 chamber, was used (Martin Christ GmbH, Germany). The procedure included the freezing of the fillets to −56.0 ± 0.1 °C, and then drying them at 0.3 mbar for 24 h. The temperature of the samples was slowly increased (0.4 °C min^{-1}) from −56.0 to 0.0 °C during the drying. As a result, the moisture content in the dried samples was in the range between 5.0% and 6.0% w.b. Then the dried fillets (5 pieces) were milled into powder. This average probe was used for further investigations. The samples with a lower moisture content were obtained by drying them at 105.0 ± 1.0 °C.

The equilibration in the climatic test chamber KMF 115 (Binder®, Germany) was used for obtaining the moisture content in the range between 5.0% and 25.0% w.b. The milled samples were equilibrated at +20.0 ± 0.1 °C, and the relative humidity varied in the range between 30.0 ± 0.2% and 90.0 ± 0.5%. This method helped to get a uniform moisture dispersion in the samples. Selecting the optimal relative humidity for the equilibration of samples in the climate chamber was based on sorption isotherms obtained with a water sorption analyzer Cisorp (CI Electronics Ltd., U.K.). A certain amount of water was added into the samples after the climatic chamber treatment with the aim to increase the moisture content up to 60.0%. The dried fish powder with different water contents were placed into plastic vials (50 mL) with hermetic lids and stored in the chilling chamber (Electrolux ERF3866AOX, Sweden) at +4.0 ± 1.0 °C.

2.2. Compressive stress experiment

The compressive stress experiment was done with an Instron Testing system model 1011 (Instron® Ltd., U.K.). The working area of the instrument was equipped with a climate chamber, which had a heat exchanger and a TS-thermocouple for temperature regulation. The liquid nitrogen was chosen as a working fluid, which gave an opportunity to decrease the temperature in the chamber to −150 °C. The compression rate equaled to 5 mm min^{-1}. The data was registered by an Instron Series IX Automated Materials Testing System version 5, and presented as strain–stress diagrams. A total of 16 samples were investigated for each temperature. For the experiment reaching temperatures below −85 °C, the samples were equilibrated in the climate chamber during the 3 h beforehand.

2.3. DSC analysis

The DSC analysis was done with a DSC Q2000 (TA Instruments, USA) equipped with a Liquid Nitrogen Cooling System (TA Instruments, USA). The temperature and cell constant calibrations were done with indium. The heat capacity was calibrated with a sapphire in the range between −150.0 and 150.0 °C. Helium was chosen as a purge gas at 25 mL min^{-1}, according to TA's instrument recommendations. The reference sample was an empty hermetically sealed aluminum pan.

The samples with masses between 7 mg and 10 mg were placed into aluminum pans with hermetic lids. The pans were sealed with a Tzero® DSC Sample Encapsulation Press (TA Instruments, USA). Then the samples were placed by an autosampler into the DSC cell.

Samples with a moisture content below 25.0% w.b. were cooled and equilibrated for 60 min at −150.0 °C; the cooling rate was 5 °C min^{-1}. Then samples were scanned to 25.0 °C with the heating rate of 5 °C min^{-1}. Samples with a moisture content above 25.0% w.b. were cooled (5 °C min^{-1}) and equilibrated at −150.0 °C for 60 min, then warmed up to −15.0 °C (5 °C min^{-1}) and equilibrated for 60 min and cooled again to −150.0 °C (5 °C min^{-1}). Such equilibration at higher temperatures after chilling is called annealing. The annealing is considered to be helpful for achieving the maximal freeze concentration and, as a consequence, avoiding exothermic peaks. But some researchers reported a glass transition in fish meat without annealing (Agustini et al., 2001; Inoue and Ishikawa, 1997; Ohkuma et al., 2008). Exothermic peaks during heating are mostly associated with the recrystallization of existing crystals, and can be found in products which contain carbohydrates or fats. For example, perfect exothermic peaks have appeared in dried tomatoes after a glass transition (Telis and Sobral, 2002). The DSC scanning to +25.0 °C was performed