GLASS TRANSITION INFLUENCE ON ICE RECRYSTALLIZATION IN ATLANTIC SALMON (*Salmo Salar*) DURING FROZEN STORAGE

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Abstract

- Low temperature transitions may occur in frozen foods due to the temperature fluctuations resulting in less viscous and partially melted food matrices;
- In the current study, the influence of glass transitions and temperature fluctuations on ice recrystallization during the frozen storage of salmon fillet was systematically investigated;
- The characteristic glass transition temperature (T_g') and onset temperature of ice crystal melting (T_m') in salmon determined using a modulated differential scanning calorimeter (MDSC) were -27 and -17ºC, respectively;
- The temperature (T = -35ºC) of frozen salmon fillets was modulated within glassy state ($T<T_g'$) and to achieve a partial-freeze-concentrated state ($T_g'<T<T_m'$) and a rubbery state ($T>T_m'$), by exposing the trays to room temperature (23ºC) for predetermined periods (2 to 26 min) twice a day during the four weeks of storage;
- The characterization of ice crystals was conducted by observing the cavities formed after sublimation of ice crystals using (a) Environmental scanning electron microscopy (ESEM) (b). *X*-ray computed tomography (XCT);
- Ice crystal growth was observed in frozen salmon in the glassy state; however the ice crystal size was greatest in the rubbery state (when the temperature fluctuation resulted in temperature above T_m');
- The findings of this study are important to the frozen food industries in optimizing the storage and distribution conditions to minimize textural quality loss due to recrystallization.

Introduction

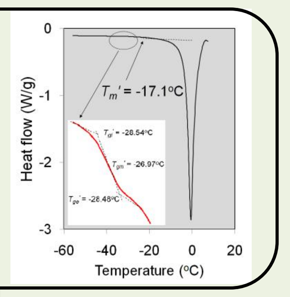
- Temperature fluctuations during storage and distribution are often unavoidable, aggravate the rate of recrystallization in frozen foods.
- Recrystallization is the process of increasing the size and shape and decreasing the number of ice crystals in frozen foods during storage (Donhowe and Hartel, 1996).
- Recrystallization causes textural changes, which adversely affect frozen food quality.
- Foods are expected to be most stable when stored in their high viscous glassy state ($10^{12\text{-}14}$ Pas), due to restricted molecular motions (Goff and Sahagian, 1996).
- Temperature fluctuations during storage and distribution may result in glass transitions and ice melting when temperatures go above characteristic glass transition (T_g') and onset of ice crystal melting (T_m') in frozen foods.
- A clear understanding of the relationship between glass transitions resulted by temperature fluctuations and rate of various diffusion limited changes such as recrystallization is still not achieved (Sablani and others 2010).
- The objective of the current study was to systematically investigate the influence of glass transitions and temperature fluctuations on ice recrystallization during storage of Atlantic salmon fillet (*Salmo salar*).

Materials and Methods

Time needed to achieve state transitions due to temperature fluctuations using **COMSOL Multiphysics**

Fresh salmon packaged in polymeric trays

T_g' of salmon = -17ºC
T_m' of salmon = -27ºC
using **Modulated Differential Scanning Calorimeter (DSC)**



Storage of salmon in trays at -35ºC (glassy state) for one month

Glassy state	Glassy ⇕ Partial-freeze-concentrated	Glassy ⇕ Rubbery	Glassy state
-35ºC ⟷ 3ºC T; $T < T_g'$	-35ºC ⟷ 13ºC T; $T_g' < T < T_m'$	-35ºC ⟷ 23ºC T; $T > T_g'$	T = -35ºC
Exposure conditions: 2 min at 23ºC twice a day	Exposure conditions: 12 min at 23ºC twice a day	Exposure conditions: 23 min at 23ºC twice a day	Product is not subjected to state transitions

Freeze drying

Shelf temperature = -25ºC
Condenser temperature = -60ºC
Drying temperature = 5ºC
Pressure = 20 Pa
Drying time = 72 h

Environmental Scanning Electron Microscopy (ESEM)

- Ice crystal size (D)

X-ray Computer Tomography (XCT)

- Percentage object volume (POV)
- Object surface/ volume ratio (OSVR)
- Degree of anisotropy (DA)

Kinetic model for ice crystal size increase in frozen salmon during storage

$$(D - D_0) = A + k\,t^{\frac{1}{n}}$$

Statistical Analysis by 2-way LSD using SAS 9.1

Results and Discussion

Effect of storage time on ice recrystallization

- In general, ice crystal size increased between 121.4-221.4 µm (82.4% increase) during frozen storage of salmon due to recrystallization depending upon the state/state transition.
- Melt-refreeze and isomass rounding were the possible mechanisms of recrystallization observed (Figure 1 and 2).
- An increase in the proportion of ice volume in frozen salmon due to crystallization as observed by an increase in POV. This increase ($p<0.05$) in POV (from 49 to 64.4) may be attributed to the conversion of unfrozen water to ice in frozen salmon during storage (Table 1).
- OSVR may be related to the shape of the ice crystals. A decrease ($p<0.05$) in OSVR (from 3.33 to 0.62) during storage may indicate a decrease in surface area or an increase in volume or both. The ice crystals become more spherical in nature resulting in their reduced surface area during storage (Table 1).
- A decrease in DA (0.97 to 0.91) of ice crystals in frozen salmon indicate the ice crystals became regular and symmetrical in shape during storage (Table 1).

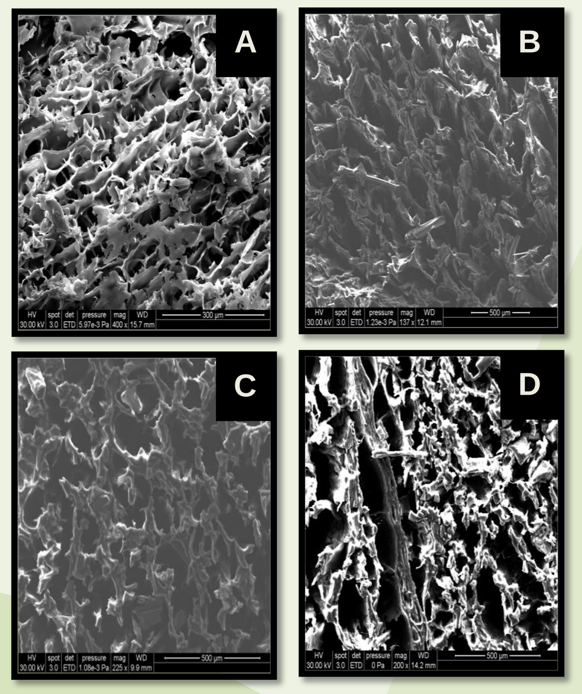


Figure 1. Scanning electron microscopy pictures of frozen salmon subjected state transitions during 4 weeks storage. (A) Salmon immediately after freezing, (B) Frozen salmon with $T < T_g'$, (C) $T_g' < T < T_m'$, (D) ($T > T_m'$).

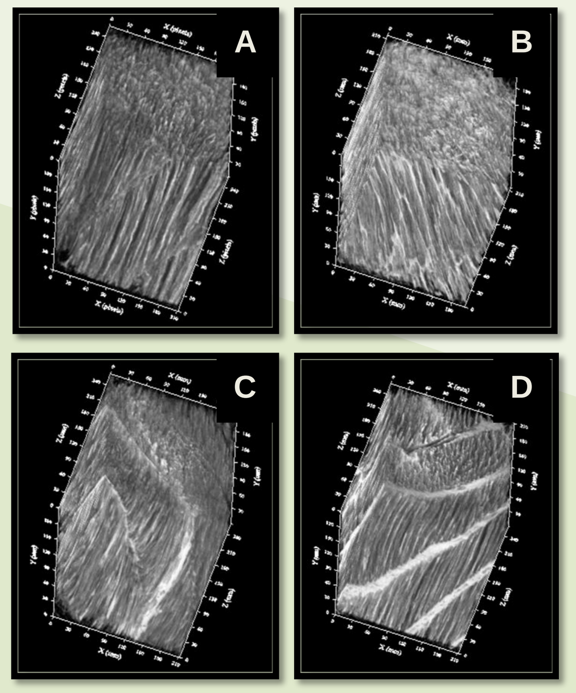


Figure 2. *X*-ray computed tomography 3D images of frozen salmon stored 4 weeks (A) ($T<T_g'$) without temperature fluctuations, (B) ($T<T_g'$) with temperature fluctuations, (C) ($T_g'<T<T_m'$), (D) ($T>T_m'$)

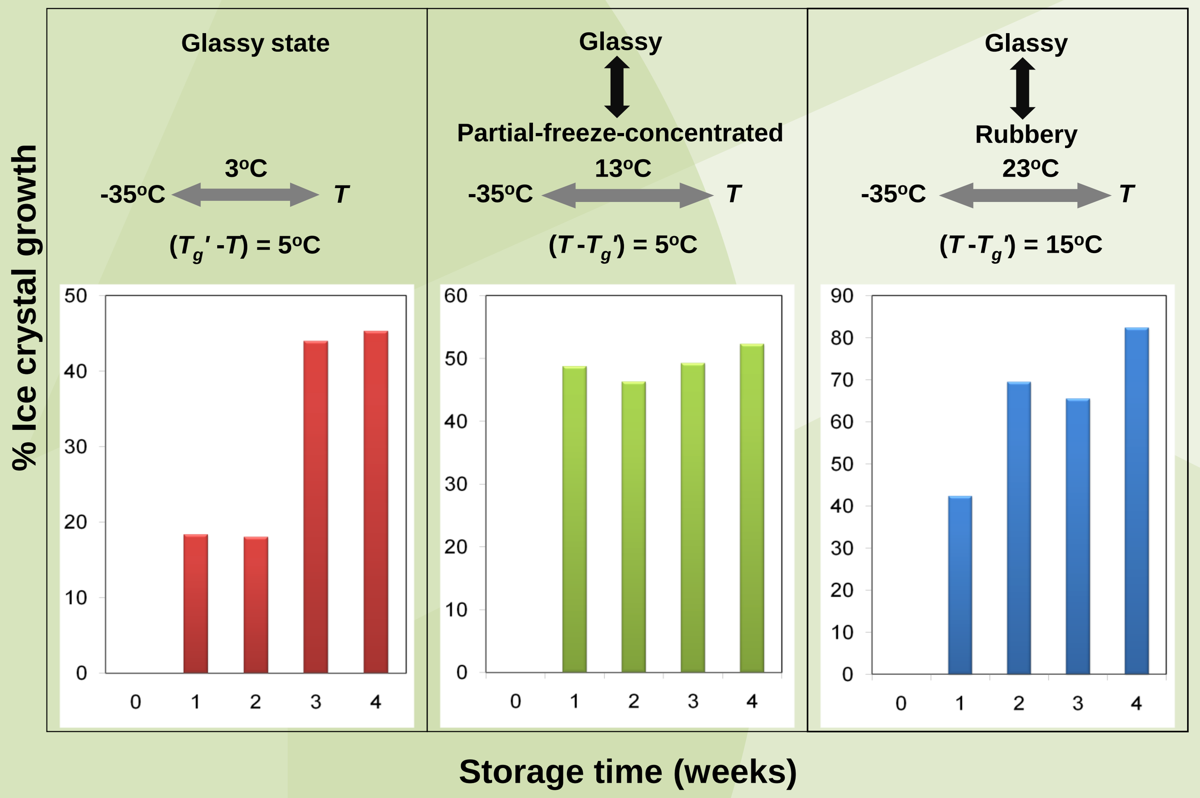


Figure 3. % growth in ice crystal size in frozen salmon subjected to fluctuations during one month storage of frozen salmon. Where T_g' = Glass transition temperature of maximally-freeze-concentrated matrix, T = Fluctuation temperature

Table 1. POV, OSVR and DA values of frozen salmon determined using *X*-ray tomography

Geometric Property	Storage time				
	0 days	28 days			
	-	No temperature fluctuation ($T < T_g'$; glassy state)	($T < T_g'$; glassy state)	($T_g' < T < T_m'$; glassy to partial-freeze-concentrated state transition)	($T > T_m'$; glassy to rubbery state transition)
Percent Object Volume, POV (%)	49±4.1	56.5±3.7	62.7±5.2	64±2.54	64.4±3.3
Object Surface/Volume Ratio, OSVR (1/µm)	3.33±0.4	0.64±0.05	0.61±0.04	0.57±0.04	0.62±0.04
Degree of Anisotropy, DA	0.97	0.96	0.83	0.84	0.91

Effect of state transitions on ice recrystallization

- The % increase in ice crystal size was significantly greater in frozen salmon with glass-to-rubber transition (82.4%) in comparison to that in frozen salmon with glass-to-partial-freeze concentrated transition (52.3%) (Figure 3).
- T_g' is relatively more important than T_m' considering the change in ice crystal size during storage.
- However, a 22.1% increase in ice crystal size was observed even in the glassy state ($<T_g'$) during storage indicating limited but continued molecular mobility within the glassy state (Figure 3).
- The POV, OSVR and DA values of ice crystals in frozen salmon with glass-to-rubber transition were not considerably different from those of frozen salmon with glass-to-partial-freeze-concentrated transition during storage (Table 1).
- T_m' may be an important temperature considering the ice crystal shape change with recrystallization.
- The recrystallization rate constants (k) obtained for frozen salmon without state transitions, glass-to-partial-freeze-concentrated transition, and glass-to-rubber transition by fitting the recrystallization data with the kinetic equation were 35.8, 40.7, and 61.5 week^{-1} respectively.
- Temperature fluctuations causing state transitions may have aggravated translational and rotational mobility of liquid water and solute molecules resulting in their increased diffusion during storage.

Final Remarks

- The ice crystal size, % ice crystal growth rate, POV values of frozen salmon with state transitions were considerably greater than those of frozen salmon without state transitions indicating the importance of T_g' and T_m' in recrystallization.
- Temperature fluctuations are often unavoidable, however, it is essential to keep the product temperature below T_g' and T_m' to avoid the texture degradation due to ice crystal growth during storage and distribution.

References

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