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original scientific paper

Model of Cryoprotectants Effect on Thermal Conductivity and Enthalpy of Surimi Prepared from Adriatic Pilchard

Dragan Kovačević and Želimir Kurtanjek

Faculty of Food Technology and Biotechnology,
University of Zagreb, Pierottijeva 6, 10 000 Zagreb, Croatia

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Summary

Determination of relative apparent specific enthalpy (H), initial freezing temperature (θ_i), and thermal conductivity (k) of surimi in the temperature range from –25 °C to +5 °C by differential thermal analysis (DTA) and a system for measurement of thermal conductivity of food by the method of unsteady responses from a line heat source are presented. Samples of surimi were prepeared in laboratory conditions from Sardina pilchardus with addition of Polydexstrose, starch, and mixture of sorbitol and sucrose (S/S) in mass ratio 1:1. Water content in surimi was 82.01% before mixing with the added substances. For interpretation of experimental results and determination of thermophysical properties mathematical models of $H(\theta)$ and $k(\theta)$ were used, while θ_i were determined from DTA curves. Values of k, H and θ_i of surimi samples were correlated with mass fractions of the added substances in the range of 0–12%. Values of $H(\theta)$ and $k(\theta)$ at freezing temperatures were dependent of a mass fraction of unfrozen water which resulted from various cryoprotectant efficiency of the added substances.

Keywords: surimi, thermophysical properties, mathematical model, DTA, line heat source method

Introduction

In surimi technology the key process is cryiostabilization of fish muscle proteins by physicochemical methods and chemical factors. Main physicochemical effects are the result of a leaching process of fish mince and most effective chemical factors are due to cryoprotection effects of mono- and disaccharides, glycitols (sugar alcohol) and dicarboxylic acids *(1)*. Estimation of quantitative cryoprotectant effects is commonly studied by DSC for measurement of enthalpy of denaturation of salt extractable proteins in the range of thermal transitions *(2–4)*. This method enables estimation of the quantity of native proteins as a function of frozen storage but does not provide specific analysis of the cryostabilization mechanism. Measurements of thermal conductivity and relative apparent specific enthalpy in the freezing range contribute to the understanding of the crystabilization mechanism. Its complexity result from: a) dynamics of intermolecular interaction of water-cryprotectants-proteins; and b) intricate process of water phase transformation. Thermal properties are mainly evidence and function of the physical and chemical state of water, especially a function of the unfrozen and frozen water ratio. Studies of Wang and Kolbe *(5)* show that an increase in cryoprotectant content results in small changes in thermal conductivity, but can be quantified and applied for correction of the parameters in the Schwartzberg model. Relative specific apparent enthalpy in the freezing range is a strong function of the unfrozen and frozen water ratio. Wang and Kolbe *(6)* showed that effect by determination of relative apparent specific enthalpy and unfrozen water mass fraction by the use of DSC method.

This work presents a study of the effect of starch addition in surimi, in addition to Polydextrose and sorbitol/sucrose (S/S) as cryoprotectants, in order to show that change of thermal properties is not only a consequence of increase in dry matter content but is an essential effect of active function of cryoprotectants on distribution of unfrozen water and dynamics of phase transition. Applied are the methods of line heat source and DTA for measurement and modeling of thermal conductivity, initial freezing point, and relative apparent specific enthalpy. Although the DTA is considered to be a semiquantitative method, by use of the new derived model, based on orthogonal collocations, its potential has been extended for enthalpy studies *(7)*.

Materials and Methods

Samples of surimi were prepared in laboratory from Adriatic pilchard *(Sardina pilchardus)* according to technique by Lee *(8)* with details given by Sych *et al. (3)*. Samples were divided into three groups and each was mixed respectively with: a) mixture of sorbitol and sucrose in mass ratio 1:1; b) Polydextrose; c) starch. Mass fractions were in the range from 0 to 12% determined as percent of total mass. In all samples was added 0.3% of sodium tripolyphosphate. Moisture content was 82.01% determined by the AOAC method *(9)* for meat products before addition of the added components. Total proteins mass fraction was 10.95% determined with 1 g samples by Kjeldahl method *(9)*; (Kjeltec System, model 1002 Distilling Unit). Samples were packaged in polyethylene bags and quickly frozen in liquid nitrogen and stored at –25 °C. Average storage time was 5 weeks before experimental treatment.

DTA apparatus was constructed in the laboratory *(7)* and was used for measurement of initial freezing temperature and relative apparent specific enthalpy in the freezing range. Thermocouples were made from Alumel-Chromel wires with 0.07 mm diameter. The standard error in calibration was 50 mK with sensitivity of 10 mK. The instruments were interfaced with a standard PC and sampling rate of 3.5 kHz was used. All data were prefiltered with 3σ rule for noise rejection prior to data analysis. Aqueous solution of $CaCl_2$, $w(CaCl_2) = 30\%$, was used as reference substance for DTA measurement. Distilled water was used as calibration substance for correction of the initial freezing point and thermal conductivity.

Measurement of thermal conductivity was performed with impulse method and a line heat source. The probe was constructed in the laboratory *(10)* based on data by Sweat *(11)*.

Results and Discussion

Experiments for measurement of thermal conductivity were conducted in the temperature range from –25 °C to 10 °C, rate of thawing was 2.5 °C h^{-1}, and with impulses in the power range of 2.25 – 4.2 W m^{-1}. Duration of impulses was from 30 to 60 s. Applied powers were lower than those used by Sweat and Haugh *(12)* and Wang and Kolbe *(5)* which was enabled by use of high sensitivity A/D conversion and resulted in reduced disturbance in distribution of unfrozen water in samples. Lower power was applied in the temperature range close to initial freezing points. Maximum amplitude in temperature was restricted to 0.6 °C in the temperature range below –10 °C and 0.3 °C in the range up to the initial freezing points. For each sample about 40 experiments were performed and in each experiment about 400 data points were taken in the range of linear temperature increase.

For determination of thermal conductivity k from experimental data obtained by the method of line heat source a mathematical model of least squares in the linear range of temperature was applied *(10)*, which is:

$$k = \frac{Q}{4 \cdot \pi} \cdot \frac{\overline{\{\ln[(t - t_o)/s]\}^2} - \overline{\ln\left[(t - t_o)/s\right]}^2}{\overline{\theta \cdot \ln\left[(t - t_o)/s\right]} - \overline{\theta} \cdot \overline{\ln\left[(t - t_o)/s\right]}} \qquad /1/$$

Thermal conductivities were determined by linear regression for the temperature range corresponding to /1/, and linearity was checked by linear coefficient of determination which was in all experiments in the range $R^2 = 0.97–0.99$. The parameters of the Schwartzberg *(13)*, k'_f and B, were estimated by the least square method from the linearized model expression given by:

$$\left(k - k_f \cdot \frac{\theta_i}{\theta}\right) = k'_f \cdot \left(1 - \frac{\theta_i}{\theta}\right) + B \cdot (\theta_i - \theta) \qquad /2/$$

In /2/ the θ_i were determined from DTA and k_f were obtained by linear regression of the data above the initial freezing point. Obtained values of the thermal conductivity are in close agreement with data of Wang and Kolbe *(5)*. Mean relative error for samples with sorbitol /sucrose is lower than 5% at temperatures below –20 °C and is about 8% in the temperature range up to the initial freezing point. Regression analysis was performed in two stages. First the parameters k'_f and B were estimated from experiments with each mass fraction of the added substances. In the second stage the parameters were correlated with the mass fraction by the linear models:

$$\begin{aligned} k'_f &= a_0 + a_1 \cdot w \\ B &= b_0 + b_1 \cdot w \end{aligned} \qquad /3/$$

The estimates of the coefficients in the linear regressions /3/ are given in Table 1. The parameter B, which is related to the linear dependence of thermal conductivity on temperature, decreases with increasing mass fraction of Polydextrose and mixture sorbitol/sucrose (Table 1) due to increased level of bound water, i.e. it is a result of cryoprotectant effect. In the case of samples with added starch, the parameters k'_f and B are not functions of concentration as starch does not show cryoprotectant effect.

Table 1. The coefficients of linear regression of the parameters k'_f and B mass fraction of the added substances

Added substance	$\frac{a_0}{W\ m^{-1}\ K^{-1}}$	$\frac{a_1}{W\ m^{-1}\ K^{-1}}$	$\frac{b_0}{W\ m^{-1}\ K^{-2}}$	$\frac{b_1}{W\ m^{-1}\ K^{-2}}$
Poly-dextrose	1.175	0.00651	0.00913	$-56.1 \cdot 10^{-6}$
S / S	1.171	0.02991	0.00813	$-987.5 \cdot 10^{-6}$
Starch	1.179	0	0.00992	0

DTA measurements are presented in Fig. 1. The results with Polydextrose are presented in Fig. 1a, the results with sorbitol/sucrose (S/S) are in Fig. 1b, and the results with starch are shown in Fig. 1c. From DTA diagrams the peak points were read off as the initial freezing temperatures. In Figs. 1a and 1b can be observed systematic shifts of the initial freezing points toward lower temperatures with increased concentration of cryoprotectants. The DTA results obtained with starch

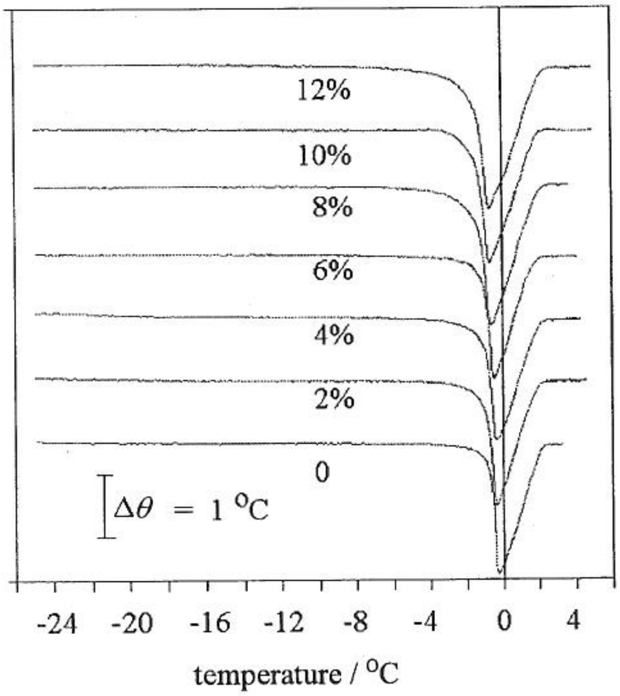

Fig. 1a. DTA curves for samples of surimi as function of mass fraction of Polydextrose

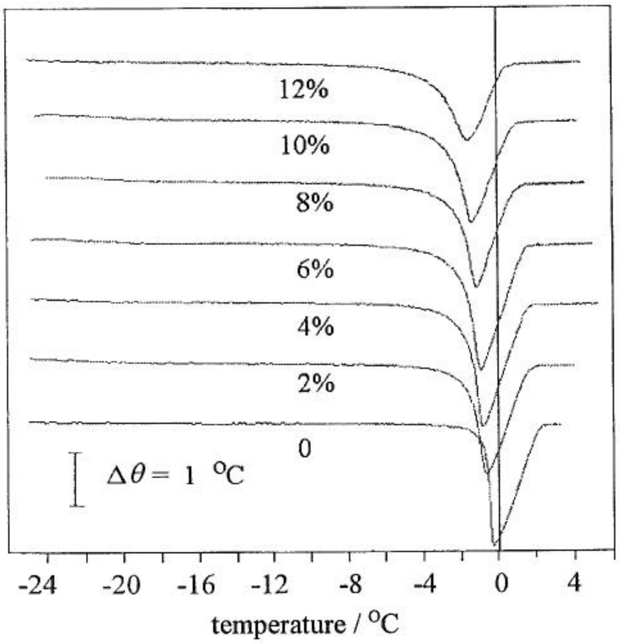

Fig. 1b. DTA curves for samples of surimi as function of mass fraction of S/S mixture

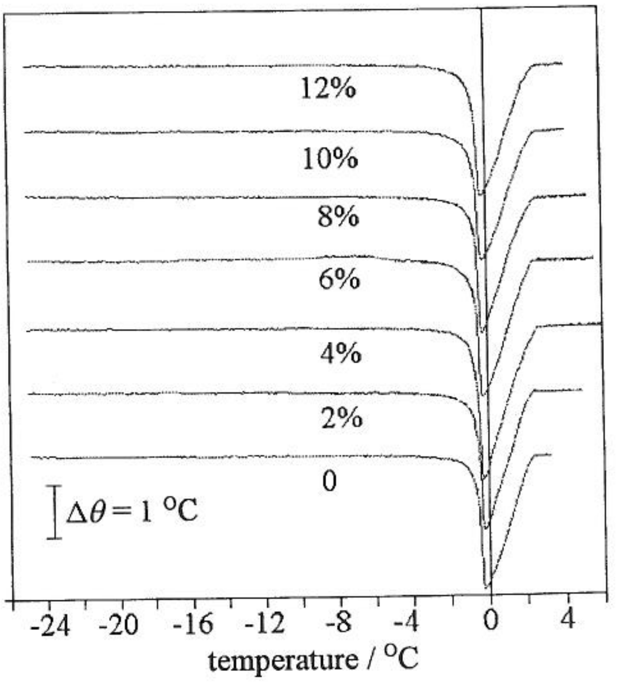

Fig. 1c. DTA curves for samples of surimi as function of mass fraction of starch

(Fig. 1c) do not exhibit functional dependence of initial freezing point on mass fraction. Below the initial freezing points DTA diagrams for samples with Polydextrose and sorbitol/sucrose show systematic increase in the temperature difference with increased level of the cryoprotectants, while the same effect is not present with the samples with starch. The effects of DTA changes shown in Figs. 1a and 1b are due to increased concentration of bound water as a result of cryoprotectant function, while experiments presented in Fig. 1 show lack of any effect of starch on DTA distribution.

Data for the initial freezing points θ_i are given in Fig. 2. Each DTA diagram is corrected only for constant error of +0.08 °C which was determined from calibration with distilled water. Linear correlations of θ_i with mass fraction of the added substances were applied which yielded:

for Polydextrose,

$$\theta_i\,/\,°\mathrm{C} = -0.282 - 0.0368 \cdot (w/\%) \qquad /4/$$

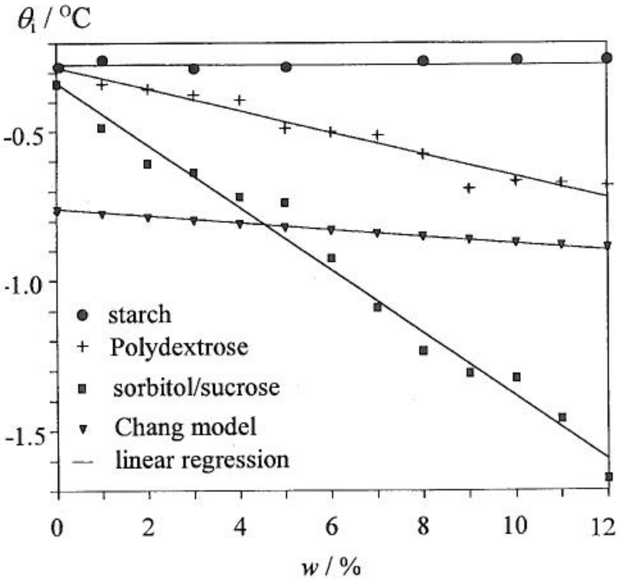

Fig. 2. Initial freezing temperatures as functions of mass fractions of the added substances

for sorbitol/sucrose (S/S)

$$\theta_i / ^\circ\mathrm{C} = -0.338 - 0.102 \cdot (w/\%) \qquad /5/$$

The difference in the slopes in /4/ and /5/ is in accordance with Raoult law by which cryoscopic freezing point decrease is inversely proportional to molecular mass. This also explains lack of decrease in θ_i for starch due to its very high molecular mass. In Fig. 2 data for $\theta_i/^\circ\mathrm{C}$ according to /5/ for samples with sorbitol/sucrose which show full agreement.

Apparent enthalpy is determined from DTA curves in intervals of 40 mK as proposed by Kovačević and Kurtanjek *(7)* which has the discrete form given by:

$$H_{k+1} = H_k + \frac{k_s(\theta_s)}{\rho_s(\theta_s) \cdot \alpha(\theta_r)} \cdot \left[\theta_{r,k+1} - \theta_{r,k} - \frac{4 \cdot \alpha(\theta_r)}{r^2} \cdot DTA_k \cdot \Delta t \right] \quad /6/$$

For the calculation the following parameters are required: thermal diffusivity of reference substance, thermal conductivity and density of samples; and continuous signals for DTA and referent temperature. The zero of relative apparent specific enthalpy is set at $\theta = -25$ °C. Thermal diffusivity of the reference substance as function of temperature was correlated from data by Ibele *(14)*:

$$\alpha(\theta) = 0.1323\ \mathrm{m^2\,s^{-1}} - 3.046 \cdot 10^{-4}\ \mathrm{m^2\,s^{-1}\,^\circ C^{-1}} \cdot \theta \quad /7/$$

Data for densities of surimi samples in frozen state are calculated from data by Zaitsev *et al. (15)* with correction for water content. Based on these data the nonlinear correlation of density with temperature is proposed here:

$$\rho_s(\theta) = 950.0\ \mathrm{kg\,m^{-3}} - 75.945\ \mathrm{kg\,m^{-3}} \cdot \left(1 - e^{0.3 \cdot \theta / ^\circ\mathrm{C}}\right) \quad /8/$$

The relative apparent specific enthalpies in the temperature range from –25 °C to initial freezing points are shown in Fig. 3.

The results are given in the mass fraction range from 0 to 12% for samples with Polydextrose, sorbitol/sucrose (S/S) and starch. To verify the method of enthalpy determination from DTA based on formula /6/ in Fig. 4 a

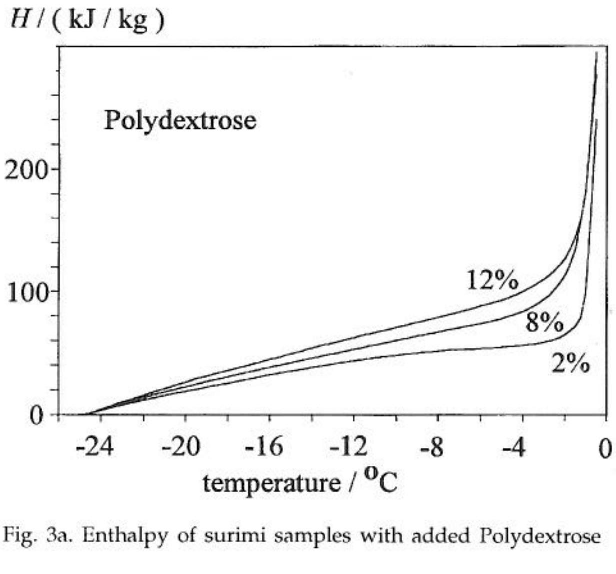

Fig. 3a. Enthalpy of surimi samples with added Polydextrose

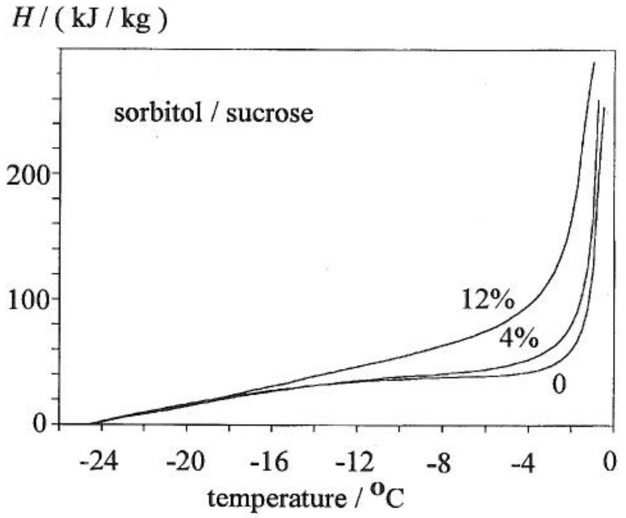

Fig. 3b. Enthalpy of surimi samples with added S/S

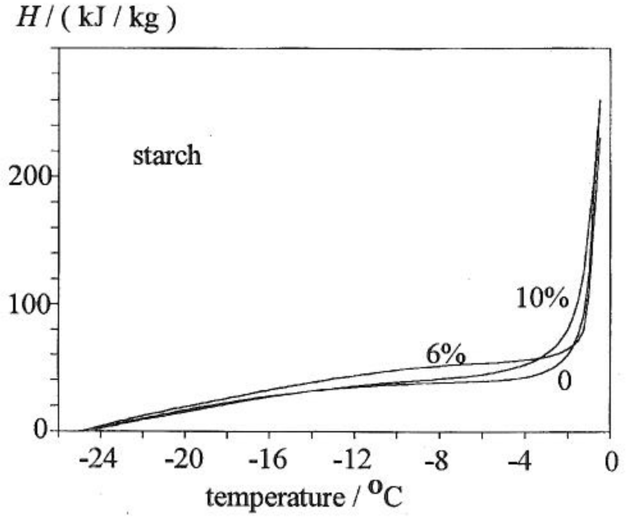

Fig. 3c. Enthalpy of surimi samples with added starch

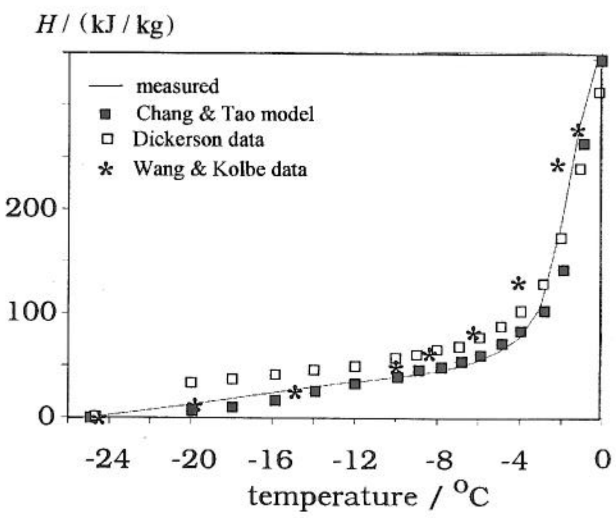

Fig. 4. Enthalpy of surimi measured by DTA, compared with data from literature

comparison is given with data from Chang and Tao *(16)* relative apparent specific enthalpy correlation for the group of meat products, Dickerson *(17)* data, and Wang and Kolbe *(6)* obtained by independent measurement with DSC method. Data from the correlation do not account for addition of cryoprotectors but all data are corrected for zero relative apparent specific enthalpy at temperature –25 °C. Differences between our data determined from DTA and literature are relatively small and can be attributed to differences in samples. Results in Figs. 3a and 3b show change in relative apparent specific enthalpy, i.e. increase at lower temperatures with increased mass fraction of the cryprotectants. For samples with mass fraction of 12% an average increase of cca. 40 kJ kg^{-1} at –4 °C is observed.

The results for samples of surimi with addition of starch in the mass fractions from 0 to 12% are presented in Fig. 3c. Starch is used in the production of "kamaboko" as it improves gel-forming ability by formation of granules which absorb water and increase elasticity and consistency of the products *(18)*. The relative apparent specific enthalpy does not change with increase of starch concentration, which confirms the results of Matsumoto and Noguchi *(1)* that it does not increase bound water content, i.e. it has no cryoprotectant effect.

Conclusion

Measurements of thermal conductivity and enthalpy of surimi give a significant insight into cryoprotectant function.

Polydextrose and sorbitol/sucrose (S/S) lower thermal conductivity and relative apparent specific enthalpy at lower temperatures while samples with the addition of starch do not show this effect. These changes are due to the cryoprotectant effect as they increase concentration of bound water in the measured temperature range from –25 °C to initial freezing points.

Functions of $H(\theta)$ and $k(\theta)$ at freezing temperatures are a result of mass fraction of unfrozen water resulting from different cryoprotectant efficiency of the added substances.

Acknowledgement

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List of symbols

Symbol	*Unit*	*Meaning*
a_o, a_1	W m^{-1} K^{-1}	parameters in regression of thermal conductivity
α	m^2 s^{-1}	thermal diffusivity
B, b_o, b_1	W m^{-1} K^{-2}	parameters in regression of thermal conductivity
$DTA(t)$	°C	difference of temperatures of sample and reference substance
H	J kg^{-1}	relative apparent specific enthalpy
k	W m^{-1} K^{-1}	thermal conductivity
k'_f, k_f	W m^{-1} K^{-1}	parameters in Schwartzberg model
Q	W m^{-1}	power per unit length
R^2		coefficient of determination
r	m	radius of a test chamber
ρ	kg m^{-3}	density
t	s	time
θ	°C	temperature
θ_i	°C	initial freezing point
w		mass fraction
Subscript		
k		sampling index
o		initial
r		reference
s		sample

References

1. J. J. Matsumoto, S. F. Noguchi, Cryostabilization of Protein in Surimi. In: *Surimi Technology*, T. Lanier, C. M. Lee (Eds.), Ch.11, Marcel Dekker Inc., New York (1992) pp. 357–388.
2. M. C. Wu, T. Akahane, T. C. Lanier, D. D. Hamann, *J. Food Sci. 50* (1985) 10.
3. J. Sych, C. Lacroix, L. T. Adambounou, F. Castaigne, *J. Food Sci. 55* (1990) 356.
4. J. W. Park, R. W. Korhonen, T. C. Lanier, *J. Food Sci. 55* (1990) 353.
5. D. Q. Wang, E. Kolbe, *J. Food Sci. 55* (1990) 1217.
6. D. Q. Wang, E. Kolbe, *J. Food. Sci. 56* (1991) 302.
7. D. Kovačević, Ž. Kurtanjek, *Prehrambeno-tehnol. biotehnol. rev. 31* (1994) 157.
8. C. M. Lee, *Food Technol. 38* (1984) 69.
9. *Official Methods of Analysis*, 10th Ed. AOAC, S. Williams (Ed.) Arlington, VA (1984) p. 153.
10. D. Kovačević, Ž. Kurtanjek, *Prehrambeno-tehnol. biotehnol. rev. 33* (1995) 31.
11. V. E. Sweat, *ASME-AIChE Heat Transfer Conference*, St. Louis, MO (1976).
12. V. E. Sweat, C. G. Haugh, *Trans. A S A E, 17* (1974) 56.
13. H. G. Schwartzberg, *Proc. of IIR*, Karlsruhe (1977) p. 303.
14. W. Ibele, Thermophysical Properties. In: *Handbook of Heat Transfer*, W. M. Rohsenow, J. P. Hartnett (Eds.), Ch.2., McGraw Hill, New York (1973).
15. Z. Zaitsev, I. Kizeveter, L. Lagunov, T. Makarova, L. Minder, V. Podsevalov: *Fish Curing and Processing*, MIR Publisher, Moscow (1969) p. 72.
16. H. D. Chang, T. C. Tao, *J. Food Sci. 46* (1981) 1493.
17. R. W. Dickerson, Thermal Properties of Foods. In: *Freezing Preservation of Foods*, 4th ed., Avi Pub. Company, Westport, CT (1969).
18. T. Suzuki: *Fish and Krill Protein. Processing Technology*, Appl. Sci. Publ., London (1981) p. 134.

Model djelovanja krioprotektora na toplinsku vodljivost i entalpiju surimija pripremljenog od *Sardina pilchardus*

Sažetak

U radu je određivana entalpija (H), početna temperatura zamrzavanja (θ_i)) i toplinska vodljivost (k) surimija u temperaturnom području od –25 °C do +5 °C, primjenom diferencijalne termičke analize (DTA) i sustava za mjerenje toplinske vodljivosti hrane primjenom nestacionarnih odziva pobuđenih impulsima iz pravocrtnog izvora topline. Surimi je pripremljen u laboratorijskim uvjetima od srdele, Sardina pilchardus, uz dodatak polidekstroze, škroba, te smjese sorbitola i saharoze (S/S) u masenom omjeru 1:1. Maseni udio vode u surimiju prije miješanja s dodanim tvarima iznosio je 82,01%. Za interpretaciju eksperimentalnih rezultata i određivanje termofizičkih svojstava upotrijebljeni su matematički modeli H(θ) i k(θ), dok su θ_i određene iz DTA-krivulja. Vrijednosti k, H i θ_i uzoraka surimija korelirane su s masenim udjelima dodanih tvari u rasponu od 0 do 12%. Vrijednosti H(θ) i k(θ) pri temperaturama zamrzavanja ovise o masenom udjelu nesmrznute vode koji je rezultat različite krioprotektorske djelotvornosti dodanih tvari.