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Enthalpy Determination of Frozen Surimi by Differential Thermal Analysis

Određivanje entalpije smrznutog iskoštenog ribljeg mesa (surimija) diferencijalnom termičkom analizom

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Summary

This work presents the results of determination of the enthalpy of frozen surimi by using the differential thermal analysis (DTA) method. Samples of surimi were prepared in laboratory conditions from Sardina pilchardus with addition of mixture of sorbitol and sucrose (S/S) in mass ratio of 1:1 and mass fraction of sodium tripolyphosphate was 0.3 %. A DTA apparatus for on-line measurement and computer monitoring with high temperature sensitivity of 10 mK and high frequency sampling rate, 3500 readings in a second, was designed. Based on quantitative analysis of DTA results a model for determination of enthalpy in temperature range from –25 °C to temperatures of initial freezing points was developed. The model is based on the application of collocation technique for numerical approximation of the partial differential equation for heat transfer. Enthalpies of the samples with mass fractions of (S/S) from 0 to 12 % were determined. The DTA analysis yielded a linear relationship between initial temperatures of freezing and mass ratio of (S/S). For the regression model value of correlation coefficient $r^2 = 0.98$ was established. Enthalpies determined by DTA are in very good agreement with data from regression models based on calorimetric measurements. Experimentally obtained functional relationship between enthalpy, temperature and mass fraction of the cryoprotective mixture shows an increase in enthalpy as a function of the level of the mixture of sorbitol and sucrose (S/S), even at temperature of –20 °C, which is due to unfrozen water resulting from the cryoprotectant function of the (S/S) mixture.

Sažetak

*U radu je određivana entalpija smrznutog »surimija« primjenom diferencijalne termičke analize (DTA). Surimi je pripremljen u laboratorijskim uvjetima od srdele, **Sardina pilchardus,** uz dodatak smjese sorbitola i saharoze (S/S) u omjeru 1:1 i natrij-tripolifosfata (w = 0,3 %). Konstruiran je DTA-uređaj za neposredno (on-line) praćenje računalom s velikom osjetljivošću mjerenja temperature od 10 mK i velikom učestološću uzorkovanja, 3500 očitavanja u sekundi. Kvantitativnom analizom rezultata DTA izveden je matematički model entalpije za područje temperatura od –25 °C do početne temperature zamrzavanja. Osnova modela je primjena postupka kolokacija za numeričku aproksimaciju parcijalne diferencijalne jednadžbe prijenosa topline. Određene su entalpije uzoraka s masenim udjelima smjese (S/S) od 0 do 12 %. Diferencijalnom termičkom analizom dobivena je linearna ovisnost početne temperature zamrzavanja o masenom udjelu smjese sorbitola i saharoze (S/S) i izveden regresijski model s korelacijskim koeficijentom $r^2 = 0,98$. Funkcionalna ovisnost entalpije o temperaturi smrznutih uzoraka pokazuje porast entalpije, već na temperaturi od –20 °C, što je posljedica nesmrznute vode zbog djelovanja krioprotektorske smjese.*

Introduction

Surimi is the Japanese name for mechanically deboned fish muscle leached with water, and with added cryoprotectors for prevention of denaturation of myofibril proteins (myosin, actin) and loss of gel- forming ability of proteins during freezing *(1)*. Most of the world production of surimi is obtained from Alaskan pollack *(Theragra Chalcogramma) (2)*. It is a commercial fish with distinguished white meat and low content of fat *(3)*. Due to increased exploitation, resources of Alaskan pollack are diminishing resulting in demand for use of other fish species for surimi production. For example, used are parts of high value fish battered during transportation and industrial manipulation, or from scraps after operations during production of fish fillets *(4)*. In Croatia, the use of Adriatic pilchard *(Sardina pilchardus)* is the most attractive for surimi production because it makes 60 % of the total fish catch *(5)*. Pilchard is a small pelagic fish with dark muscle meat with high content of: fat (mostly unsaturated fatty acids), glycogen (in case of fast reduction of pH after death), and sarcoplasmic muscle proteins *(6)*. By use of adequate techniques, white surimi can be produced from pilchard of the A quality grade, like the one produced from Alaskan pollack *(3)*.

The process of leaching of minced meat and addition of cryoprotectors retains the ability of proteins for gel-formation during storage, at temperatures below –20 °C *(6)*, enable production from surimi of a wide spectrum of different highly demanded products such as: fish sausage, kamboko, fish burgers, fish rolls, fish pies *(7)*; and extruded products like crab and shellfish analogues, and other shelf-stable snack products *(8)*.

The most effective cryoprotectors are mono- and disaccharides, glycitols (sugar alcohol) and dicarboxylic acids *(7)*. Their function is explained by the action of the essential groups –COOH and –OH which form hydrogen bonds with dipolar molecules of water on one side, and with protein polar side chains on the other side. It results in prevention of dehydration process, intermolecular reactions of protein functional groups, and production of undesired secondary products (coagulation process) *(7,9,10)*. At the same time, the cryoprotectors slow down, or completely stop, migration of water in the vicinity of proteins preventing growth of ice crystals and limiting their size. It also limits solute concentration and their activity *(9)*.

Commercial surimi is produced with 8 % mass fraction mixture of sorbitol/sucrose in mass ratio of 1:1 *(11)*. Although water solution of sorbitol, w(sorbitol) = 70 %, has an equivalent cryoprotecting effect, better dispersion properties in the products and a lower price than the mixture of sorbitol and sucrose, it is still not being applied in industry *(12)*. Mixture of sorbitol/sucrose has been long considered as the best cryoprotector, but the latest investigations show that the same properties are achieved with low-calorie polysaccharides (Polydextrose ®, Palatinit ®, and Lactitol) which eliminate sweet flavor of final products and stimulate laxative effects *(7,9,13)*.

The aim of this work was twofold: 1) improvement of DTA technique of measurement and data analysis based on the mathematical model of heat transfer by use of collocation technique, and 2) a study of cryoprotecting effects of mixture of sorbitol/sucrose in surimi prepared from *Sardina pilchardus* and determination of enthalpy function by use of DTA technique.

Materials and Methods

Experiments were conducted with samples of surimi prepared according to the recipe *(14,15)* with added mixture of sorbitol/sucrose in the ratio 1:1 and mass fraction of 0.3 % sodium tripolyphosphate. The mixture of carbohydrates was added in the following mass fractions: 0, 4, 6, 8, 10, 12 %. Samples of surimi were prepared from pilchards from middle Adriatic sea. Preparations of samples were performed in laboratory according to a modified industrial procedure *(16)*. The procedure is based on the technique of Lee 1984 *(1)* with details given in *(9)*. Moisture content was determined by the AOAC method for meat products *(17)*, and value of 82.01 % was obtained before addition of the cryoprotective mixture. Total proteins were determined in 1 g samples of surimi by the method of Kjeldahl *(17)*; (Kjeltec System, model 1002 Distilling Unit) and the value obtained was 10.95 %. Samples were packaged in polyethylene bags and quickly frozen in liquid nitrogen and stored at temperature –(20 ± 2) °C. Average storage time of samples before experimental treatment was 5 weeks.

As reference substance for DTA measurements water solution of $CaCl_2$, $w(CaCl_2) = 30\ \%$ was used. For each experiment a sample of 1 g of surimi was placed in the test chamber with careful manipulation to avoid presence of air bubbles in the material. The cylinder with a sample and reference was quickly cooled by immersion in liquid nitrogen until temperature of –40 °C was reached. Upon cooling, the cylinder was placed in an insulation block. During experiments temperatures of the sample and reference substance were measured and a constant rate of 15 °C/h temperature increase was maintained. Heat transfer to the measurement block was not controlled. Temperature was recorded until +5 °C was reached. For each sample of the cryoprotector mixture three parallel experiments were performed.

DTA Apparatus

For DTA measurements a laboratory apparatus shown in Fig. 1 was constructed. The construction of the apparatus was based on recommendations from the literature *(18,19,20)*. The measurement block was made of brass with diameter of 46 mm and height of 70 mm. In the cylinder two test chambers were drilled with diameter of 7 mm and a depth of 45 mm (volume cca. 1 mL).

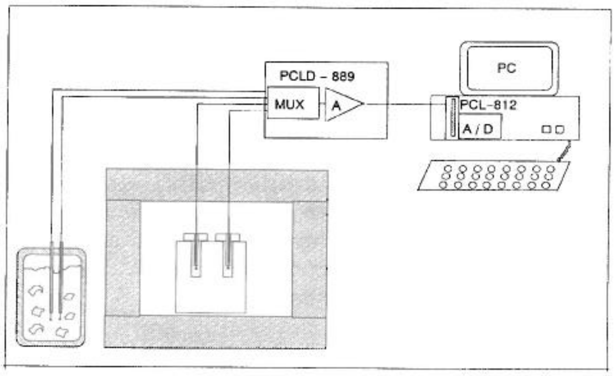

Fig. 1. Experimental system for DTA measurements. The electronic hardware components are: on PCLD-889 board are MUX-multiplexer and A-instrumentation amplifier, and the analog to digital converter (A/D) on PCL-812 board.

Slika 1. Mjerni sustav za DTA. Elektroničke komponente su: PCLD-889 ploča s multipleksérom MUX i instrumentacijskim pojačalom A, i analogno digitalni pretvornik na ploči PCL-812.

The test and reference chambers were identical and are not depicted separately in Fig. 1. The ratio between the radius and height of the working volume of the chambers is 1:10 which enables simplification of mathematical model for heat transfer as a one dimensional process. Temperatures were measured by »inhouse constructed thermocouples« made of Chromel and Alumel alloys. The thermocouple wires were 0.07 mm in diameter. Since the ratio of the thermocouple wires and sample was 1:100 it can be assumed that temperature sensors do not disturb temperature profiles, and due to negligible mass of sensors time delays are avoided. The thermocouple tip was placed in the middle of a test chamber and was kept in the position by a holder made of a steel needle. The mass ratio between the measurement block and sample was 1000:1 resulting in negligible feedback effect of latent heat on temperature distribution in the measurement block. Upon immersion of the measurement block in liquid nitrogen the block was placed in an insulation box with dimensions of 25 × 30 × 35 cm and wall thickness of 5 cm made of expanded polystyrene. The referent junctions of the thermocouples were kept in a thermos bottle with a mixture of fine particles of ice and tap water. Referent temperature was 0 °C during experiments and was monitored by a separate thermometer.

Thermocouple electromotive force (EMF) was amplified, sampled by A/D converter and on-line measured on standard PC. The electrical circuit (shown in Fig. 1.) consisted of an onboard multiplexer, instrumentation amplifier (PCLD-889) and a 12 bit A/D converter (PCL-821), Advantech Co., Ltd. The measurement range was from –25 to 25 °C. Standard error in calibration of the thermocouple was 50 mK, with sensitivity of measurements equal to 10 mK. The sampling rate of the signals was 3500 readouts per second per channel. Each batch of data was preprocessed for statistical noise rejection. For each batch of 3500 data the average and standard deviation were computed, followed by data filtering with 3-standard-deviations rejection level. The reduced set of data was recalculated for the average, and improved estimates of mathematical expectations were recorded on a computer disc in intervals of 10 seconds. For each experiment 500 records of time, temperatures of sample and referent substance were recorded as ASCII files. Data files can be transferred to standard PC software for numerical evaluation and graphical presentation.

Mathematical model of DTA

Mathematical model of DTA has been developed for quantitative determination of enthalpy of surimi in temperature range from –25 °C to initial temperatures of freezing. The model was derived from the heat balance equations for sample and reference substance. The balance for sample material is expressed by apparent enthalpy per unit mass *(H)* and thermal conductivity k_s, and is given by:

$$\frac{\partial}{\partial t}(\rho_s \cdot H) = \frac{1}{r}\cdot\frac{\partial}{\partial r}\left[k_s(T_s)\cdot r\cdot\frac{\partial T_s}{\partial r}\right] \qquad /1/$$

where dependence of sample thermal conductivity on temperature T_s is taken into account. The heat balance equation for reference substance is expressed by thermophysical parameters (specific heat capacity c_{pr} and thermal conductivity k_r) as functions of temperature T_r:

$$\frac{\partial}{\partial t}(\rho_r \cdot c_{pr} \cdot T_r) = \frac{1}{r}\cdot\frac{\partial}{\partial r}\left[k_r(T_r)\cdot r\cdot\frac{\partial T_r}{\partial r}\right] \qquad /2/$$

The both equations have the same boundary conditions: at the wall

$$T_s(t,R) = T_r(t,R) = T_W(t) \qquad /3/$$

in the center:

$$\frac{\partial}{\partial r}T_s(t,r=0) = \frac{\partial}{\partial r}T_r(t,r=0) = 0 \qquad /4/$$

and the initial conditions:

$$T_s(t=0,r) = T_r(t=0,r) = T_i \qquad /5/$$

For sample and reference the same boundary conditions and the heat transfer equation are applied assuming negligible convective effects.

The spatial components of the balance equations /1/ and /2/ can be transformed by employing the fact that temperature profiles are even functions with respect to distance. The transformation is obtained by introduction of the new dimensionless spatial variable x:

$$x = \left(\frac{r}{R}\right)^2 \qquad /6/$$

After differentiation, the spatial component of the balance equation becomes:

$$\frac{4}{R^2}\cdot\left[k(T)\cdot\left(\frac{\partial T}{\partial x}+x\cdot\frac{\partial^2 T}{\partial x^2}\right)+\frac{dk}{dT}\cdot x\cdot\left(\frac{\partial T}{\partial x}\right)^2\right] \qquad /7/$$

Due to the dependence of parameters on temperature, the balance results in a second order nonlinear partial differential equatio (PDE). The mathematical problem of quantitative DTA analysis can be stated as follows:

Given are temperatures of sample and reference substance, measured in centers $T_s(t,r=0)$ and $T_r(t,r=0)$. For a reference substance all thermophysical properties as functions of temperature are known, and so is the thermal conductivity of a sample $k_s(T_s)$, but the boundary condition $T_w(t)$ is unknown.

From solutions of the balances /1/ and /2/ dependence of apparent enthalpy H of a sample on temperature needs to be evaluated.

In general, from the mathematical point of view, the problem is complex and would require a model based on finite-elements technique. However, under experimental conditions for DTA measurements which are characterized by slow wall temperature increase at constant rate, it can be assumed that heat transfer is in a quasi-steady state. This allows simple approximate spatial discretization based on the collocation technique *(21)*.

The simplest form of solution is obtained with two collocation points selected at the center ($x_1 = 0$) and the wall ($x_2 = 1$), thus giving a parabolic profile of temperature across sample and reference substances. Using the two collocation point discretization, the solution is given in the form:

$$T(t,x) = T_1(t) \cdot l_1(x) + T_2(t) \cdot l_2(x) \qquad /8/$$

After substitution of the corresponding Lagrange polynomials $l_i(x)$ and subsequent differentiation, the expression /7/ becomes:

$$\frac{4}{R^2} \cdot \left[k \cdot (T_2 - T_1) + x \cdot \frac{dk}{dT} \cdot (T_2 - T_1)^2 \right] \qquad /9/$$

The temperature at the second collocation point is equal to the wall temperature, assuming negligible heat resistance between the brass block and substances, $T_2 = T_w$. The dynamic balance equations are solved by setting the residue of the approximation of the PDE equations /1/ and /2/ equal to zero at the center. For a reference substance the PDE is transformed to first order nonlinear ordinary differential equation (ODE) given by:

$$\frac{dT_r}{dt} = \frac{4 \cdot \alpha_r(T_r)}{R^2} \cdot (T_w - T_r) \qquad /10/$$

and for a sample substance the equation becomes:

$$\rho_s(T_s) \cdot \frac{dH(T_s)}{dt} = \frac{4 \cdot k_s(T_s)}{R^2} \cdot (T_w - T_s) \qquad /11/$$

The equation /10/ can be rearranged to give temperature of the reference material:

$$T_r = T_w - \frac{R^2}{4 \cdot \alpha_r(T_r)} \cdot \frac{dT_r}{dt} \qquad /12/$$

The above relations express the fact that temperature of the reference material lags for a constant time behind wall temperature when temperature increases at constant rate and thermal diffusivity is constant. In variable conditions the equation /11/ has to be used for calculations of the temperature difference.

Differential of enthalpy is derived by obtaining the ratio of /11/ and /10/ followed by substitution of /12/ it becomes:

$$dH = \frac{k_s(T_s)}{\rho_s(T_s) \cdot \alpha_r(T_r)} \cdot \left[dT_r - \frac{4 \cdot \alpha_r}{R^2} \cdot DTA(t) \cdot dt \right] \qquad /13/$$

where the measurement signals varying with time are: temperature of a reference substance $T_r(t)$ and the difference between temperature of sample and reference material denoted by DTA(t):

$$DTA(t) = T_s(t) - T_r(t) \qquad /14/$$

The equation /13/ for calculations is applied in its discrete form with application of a constant sampling period Δt:

$$H_{k+1} = H_k + \frac{k_s(T_s)}{\rho_s(T_s) \cdot \alpha(T_r)} \cdot$$

$$\cdot \left[T_{r,k+1} - T_{r,k} - \frac{4 \cdot \alpha(T_r)}{R^2} \cdot DTA_k \cdot \Delta t \right] \qquad /15/$$

For evaluation of /15/ are required: mathematical model for thermal diffusivity of reference substance, density and thermal conductivity of sample. As reference substance solution of $CaCl_2$, $w(CaCl_2) = 30$ % was used, which has freezing temperature below –25 °C and its thermal diffusivity is a linear function of temperature. From the data for thermal properties *(22)* for temperature range from –25 do +25 °C thermal diffusivities were calculated and linear regression was obtained:

$$\alpha_r(T) = a_o + a_1 \cdot T \qquad /16/$$

where the coefficients have values $a_o = 0.1323$ mm^2 s^{-1}, $a_1 = 3.046 \cdot 10^{-4}$ mm^2 s^{-1} K^{-1}, and correlation coefficient is $r^2 = 0.99$. Nonlinear regression model proposed by Schwartzberg *(23)* with modification for surimi by D. Wang and E. Kolbe *(14,15)* was used for thermal conductivity of surimi:

$$k(T) = k_1 + k_2 \cdot (T_f - T) + (k_o - k_1) \cdot \left(\frac{T_o - T_f}{T_o - T} \right) \qquad /17/$$

The parameters k_i are calculated from regression model:

k_o/W m^{-1} K^{-1} = 0.494
k_1/W m^{-1} K^{-1} = 1.0982 + 1.943 $\cdot w$
k_2/W m^{-1} K^{-2} = 0.009464 – 0.059 $\cdot w$

where w is mass fraction of the cryoprotector mixture.

Data for densities at temperatures in the range from 0 do –25 °C are obtained according to Zaitsev *et al. (24)*, from which a nonlinear model is proposed here:

$$\rho_s(T) = \rho_o - \rho_1 \cdot (1 - \exp(\beta \cdot T)) \qquad /18/$$

with the following values of the parameters:

ρ_o = 950.0 kg m^{-3}
ρ_1 = 75.945 kg m^{-3}
β = 0.3 K^{-1}

Results and Discussion

For the purpose of this work surimi was prepared from Adriatic pilchards by a modified procedure suitable for laboratory conditions. Mass fraction of water before addition of cryoprotective mixture was 82.01 %, and in the mixtures it was in the range from 79.85 to 81.29 %. Moisture content in the tested samples was in the range specified for high grade surimi produced on factory ships and for on shore production (9). The used cryoprotective mixture contained sodium tripolyphosphate, w = 0.3 %, which acts with sugars to enhance their cryoprotective performance by buffering the mixture and/or by chelation of metal ions *(7)*.

The design of the DTA apparatus is in agreement with assumptions on which the mathematical model for the quantitative determination of apparent enthalpy is applied. The geometry of the test chambers enables one dimensional treatment of heat transfer process. Slow rate of temperature increase of 15 °C h^{-1} makes applicable quasi-steady state approximations, and gives well defined and reproducible DTA diagrams. The use of very sensitive measurement circuit for temperature and on-line connection with a PC gave important advantages for numerical treatment of data. Use of the very high sampling rate with statistical rejection of outlayers gave data logs for accurate calculation of enthalpy during entire courses of experiments.

Data of DTA measurements stored on computer files were processed by a standard PC worksheet software for graphical presentation. Typical results obtained for mass fraction of cryoprotective mixture from 0 to 12 % are presented in Fig. 2.

The DTA curves have negligible noise, due to high sampling and statistical noise rejection, and are reproducible. The base lines of DTA curves are always in the range from 0 to 0.2 °C indicating well matched thermal properties of sample and reference. The small deviation of the base lines from 0 is the result of adjustment of thermal diffusivity of reference substance and samples. The average diffusivity in the temperature range from 20 to 0 °C of fish in frozen state *(24)* is α = 0.17 $mm^2\,s^{-1}$, and of $CaCl_2$ solution, w($CaCl_2$) = 30 %, was α = 0.12 $mm^2\,s^{-1}$ *(22)*. The peaks have exponential form on the down-fall side and steep step-like change on the up-rise side. The effect of increase of mass fraction of the cryoprotective mixture is a shift of the DTA peaks to lower temperatures and their broadening.

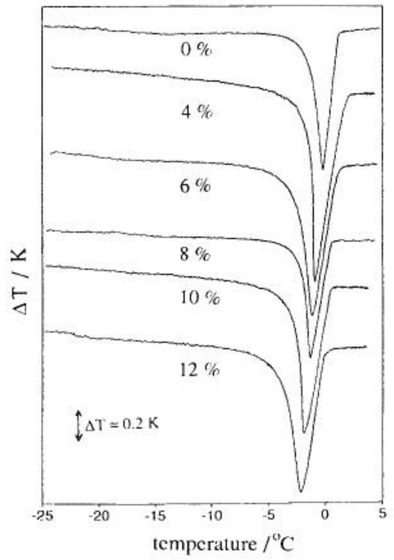

Fig. 2. DTA diagrams obtained for samples with mass fractions of the cryoprotecting mixture (sorbitol/sucrose), from 0 to 12 %, and with addition of sodium tripolyphosphate, w = 0.3 %.

Slika 2. DTA-dijagrami uzoraka s masenim udjelima krioprotektorske smjese (sorbitol/saharoza) od 0 do 12 %, s dodatkom natrij-tripolifosfata, w = 0.3 %.

Points of initial freezing T_f taken as the top points of peaks, as suggested in (25), were determined from the DTA curves. The results are shown in Fig. 3. The initial freezing points are correlated with mass ratio of the cryoprotective mixture in the samples. A linear correlation is derived:

$$T_f/K = 273.12 - 0.10224 \cdot w \qquad /19/$$

with the standard error e = 0.052 K and the correlation coefficient r^2 = 0.98, where w is mass fraction of the cryoprotector mixture. The linearity of initial point of freezing and mass fraction of solid matter in foods has been shown in *(25,26)*, and also has been proven for content of cryoprotective mixture in surimi *(14)*. The depression of freezing points with the increase of fraction of cryoprotective mixture results from cryoscopic effect and linearity is confirmed by Rault's law.

In Fig. 4. are presented enthalpies of surimi samples with increasing levels of the cryoprotective mixture. The data were obtained by the mathematical model of DTA measurements and the expression /15/ has been used for calculations. The calculation procedure was applied on worksheet files with DTA data and enthalpies were obtained for all entries in a file. The enthalpy data were calculated in time increments of 10 s and are presented as continuous curves as function of the sample temperatures. The given values are apparent enthalpies resulting from sensible enthalpy (related to temperature) and phase transformation (latent heat). The zero value for enthalpy is set at temperature –25 °C. The obtained results for enthalpy are also verified by an independent experimental method, i.e. by differential scanning calorimetry (DSC) measurements conducted by Wang and Kolbe *(15)*. In Fig. 5. are given experimental values for enthalpy determined by DTA, for surimi samples without the

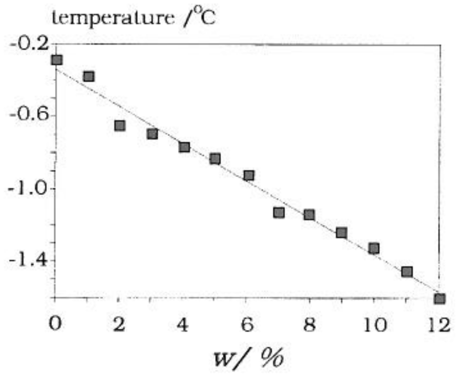

Fig. 3. Dependence of initial freezing points T_f of surimi on mass fractions, w, of the cryoprotecting mixture (sorbitol/sucrose) and addition of sodium tripolyphosphate, w = 0.3 %. With ■ are denoted experimental values obtained as peaks of DTA curves, and —— is the linear regression of T_f and w.

Slika 3. Ovisnost početne temperature zamrzavanja T_f surimija o masenom udjelu w krioprotektorske smjese uz dodatak natrij-tripolifosfata, w = 0.3 %. Eksperimentalne vrijednosti T_f očitane su kao vrhovi DTA-krivulja i označeni su s ■, a linearni regresijski model T_f i w prikazan je s —— .

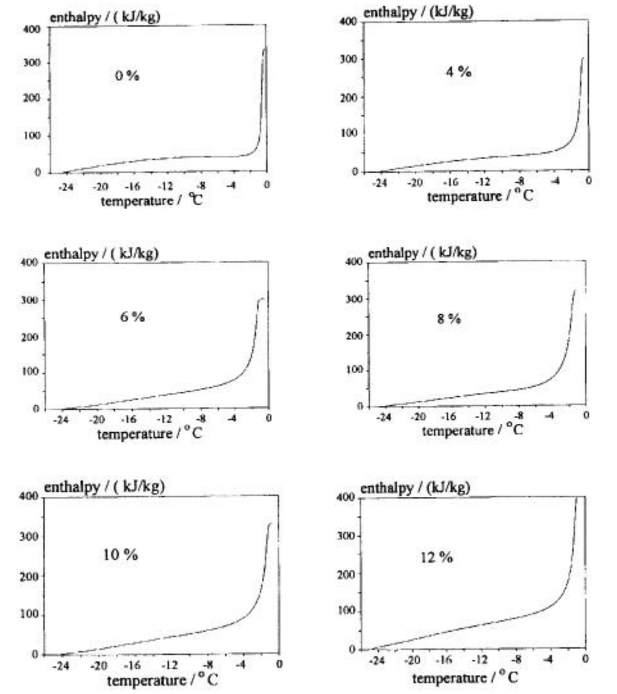

Fig. 4. Graphical representation of enthalpy *H* of surimi as function of temperature and mass fraction of the cryoprotecting mixture expressed in %. The functions are derived from DTA measurements.

Slika 4. Grafički prikazi funkcije entalpije surimija H u ovisnosti o temperaturi i masenom udjelu krioprotektorske smjese izražene u %. Funkcije su određene iz DTA-mjerenja.

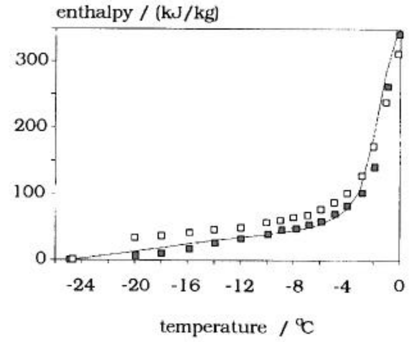

Fig. 5. Comparison of measured values of enthalpy of surimi without cryoprotecting mixture with data obtained by correlation models. With —— is denoted the enthalpy obtained by DTA measurement, □ are data given by Dickerson *(27)*, and ■ are data by Chang and Tao *(26)*.

Slika 5. Usporedba izmjerenih vrijednosti entalpije »surimija« bez dodatka krioprotektorske smjese s podacima određenim iz korelacijskih modela. Rezultati mjerenja s DTA prikazani su s ——, Dickersonovi podaci *(27)* dani su s □, a rezultati Chang i Tao-a *(26)* s ■.

cryoprotecting mixture, together with correlation data from the Chang and Tao *(26)* and Dickerson *(27)*. Their correlations is given by

$$H_r = b_1 \cdot T_r + (1 - b_1) \cdot T_r^{b_2} \qquad /20/$$

$$H_r = \frac{H}{H_f} \qquad T_r = \frac{T - 227.6\ \text{K}}{T_f - 227.6\ \text{K}}$$

The parameters b_1 = 0.295 and b_2 = 22.455 were recalculated by the models *(26)* proposed for meat group products with experimentally determined mass fraction of water in surimi samples. Data by Dickerson are taken from the table *(27)* for fish and meat cod. By comparison it can be concluded that enthalpies determined by DTA are in very good qualitative and quantitative agreement with data from the given correlations.

Increase in enthalpy with increasing levels of the additive mixture is a result of the cryoprotective effect. In the measured range from –25 °C to initial freezing points due to the cryoprotectors there is an increase in the amount of bound water. Fraction of bound water increases with the amount of the additive mixture, resulting in increase in enthalpy due to required latent heat for phase transformation below the intial freezing point. The phenomenon can be explained by interaction of hydroxyl groups of cryoprotector molecules with water molecules and dissociated groups of proteins. This also leads to increased level of »unfreezable« water *(27)*, *(28)* which at usual storage temperatures below –20 °C does not freeze. Presence of bound water limits migration of water molecules from the surroundings of myofibrilar proteins, slows growth of ice crystals and decreases the amount of frozen water. A consequence of these processes is the formation of small ice crystals and protection of water layer between protein molecules, which acts as mechanical barrier for protein aggregation *(7)*. Continuous concentration of dissolved substances, due to crystallization of water during freezing, results in further lowering of freezing point, which is especially pronounced in close surroundings of proteins, where due to electrostatic forces most of the cryoprotector molecules are present. Intensity of the described mechanisms of cryoprotective effects can be quantitatively monitored by enthalpy change. Values and courses of change of enthalpy during thawing are closely related to physicochemical state of water and entropy of the system. It is also a consequence of formation of small ice crystals which have lower melting *(29)* temperature. The steepest increase in enthalpy is observed with the sample containing w = 12 % of the (S/S) mixture. This sample has at each temperature the highest level of unfrozen water observed as highest enthalpy, and also a maximum decrease of initial freezing point.

Conclusion

A laboratory apparatus for DTA measurements with on-line monitoring and data processing by a standard PC was designed. High sampling rate and applied statistical noise rejection enable reproducible and accurate experiments.

Experiments were conducted with surimi prepared in laboratory conditions from *Sardina pilchardus* with addition of the cryoprotectors. From analysis of DTA curves initial freezing points were determined which obey linear dependence on mass fraction of cryoprotectors and decrease with its level.

A mathematical model was developed for heat transfer processes in sample and reference substance by use of collocation technique. Quantitative treatment of DTA curves has provided enthalpies of surimi in the temperature range from –25 °C to initial freezing points. Enthalpy determined by DTA was verified by data from correlation models based on calorimetric measurements.

Value and distribution of enthalpy reflects the state of water resulting from effects of the cryoprotectants in surimi. It has been demonstrated that quantitative treatment of DTA by mathematical modeling can provide insight into molecular interaction between cryoprotectants, water and proteins.

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List of symbols
Popis oznaka

Symbol Oznaka	Unit Jedinica	Meaning Značenje
a_o, a_1	$m^2\,s^{-1}$, $m^2\,s^{-1}\,K^{-1}$	parameters in the model for thermal diffusivity parametri u modelu toplinske difuzije
α	$m^2\,s^{-1}$	thermal diffusivity toplinska difuznost
b_1, b_2		model parameters for enthalpy parametri modela za entalpiju
β	K^{-1}	parameter in the model for density parametar u modelu za gustoću
c_n	$J\,kg^{-1}\,K^{-1}$	specific heat capacity at constant pressure specifična toplina pri stalnom tlaku
e		standard error standardna pogreška
DTA(t)	°C	difference of sample and reference temperature razlika temperature uzorka i referentnog materijala
H	$J\,kg^{-1}$	apparent enthalpy prividna entalpija
k	$W\,m^{-1}\,K^{-1}$	thermal conductivity koeficijent toplinske vodljivosti
k_o, k_1	$W\,m^{-1}\,K^{-1}$	parameters in the model of thermal conductivity
k_2	$W\,m^{-1}\,K^{-2}$	parametri u modelu toplinske vodljivosti
$l_j(x)$		j-th Lagrange interpolation polynomial j-ti Lagrangeov interpolacijski polinom
r	mm	radius radijus
R	m	radius of the test chamber radijus mjernog udubljenja
r^2		correlation coefficient koeficijent korelacije
ρ	$kg\,m^{-3}$	density gustoća
t	s	time vrijeme
Δt	s	sampling period vrijeme uzorkovanja
T	K	temperature temperatura
T_o	K	water triple point trojna točka vode
x		relative distance relativna udaljenost
w		mass fraction maseni udio

Subscript
Indeks

i	initial početno
j	index of Langrange polynomial indeks Lagrangeovog polinoma
k	sampling index indeks uzorka
f	initial freezing početak zamrzavanja
r	reference referentno
s	sample uzorak
w	wall stijenka

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