CRYOPROTECTIVE EFFECTS OF POLYDEXTROSE AND K-CARRAGEENAN ON PILCHARD SURIMI

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SUMMARY

Initial freezing points (T_i) of surimi samples prepared from Sardina philchardus mixed with sodium tripolyphosphate (w = 0.3%), κ - carrageenan (w = 0.5%) and different mass fractions of polydextrose (w = 1 -10%) were determined by use of differential thermal analysis (DTA). On-line connection between measuring instrument and a computer made possible direct monitoring of thawing process of the sample with high temperature sensitivity (10 mK), frequency sampling rate (3.5 kHz) and statistical filtration of measured temperature and graphic interpretation of the results. Water content in surimi was 79.05% before mixing with the added substances. The initial freezing point of surimi samples were determined from the DTA curves. Relations between decreases of the initial freezing point T_i as function of mass fractions of the added substances w were determined by linear regression. Coefficients of determination R^2 = 0.62 were determined for all samples of surimi mixed with κ - carrageenan and different mass fractions of polydextrose. The largest effect of cryoscopic depression on the initial freezing point T_i was found in the samples of surimi with added κ - carrageenan (w = 0.5%) and polydextrose (w = 10%), with the value of - 2.75 °C. The results were compared and discussed with the literature data.

Key words: *Initial freezing point, DTA, surimi, polydextrose, κ - carrageenan*

INTRODUCTION

Surimi is a Japanese name for a semi-product obtained by mechanical deboning and washing of fish meat, to which different cryoprotectants have been added to protect myofibrillar proteins from freeze-denaturation and loss of gelling capacity during frozen storage (Lee, 1984). Cryoprotectants are the substances that reduce the surface tension of water leading to slower growth of ice crystals during freezing process (Thawornchinsombut and Park, 2006). Also, they increase the mass fraction of bound (unfreezable) water, which, at the commercial freezing temperatures, acts as a mechanical barrier and prevents the coagulation of functional proteins. Monosaccharides, disaccharides, sugar alcohols and polysaccharides (polydextrose and carrageenan) are the most effective cryoprotectants (Tornaniak et al., 1998; Herrera and Mackie, 2003). The most important thermal property of food in frozen state is the initial freezing point (T_i), and it represents the temperature at which ends the first phase of water crystallisation, i.e. the phase of nucleation or formation of crystallisation nuclei, and starts the phase II, i.e. the development of ice crystals. Most mathematical models for predicting thermal property of frozen food are based on cryoscopic equation for freezing point depression (Pham, 1996; van der Sman and Boer, 2004; James et al., 2005; Boonsupthip and Heldman, 2007). It can be also defined as the temperature of the initial phase change characterised by exothermal solidification reaction, accompanied by the release of latent heat of crystallisation. The lower the initial freezing point, the more microbiologically stable the food (Miles et al., 1997). Polydextrose is a highly branched polysaccharide obtained by thermal polymerisation of glucose with citric acid as catalyser and sorbitol as plasticizer. κ-carrageenan is an anionic sulphated polysaccharide, extracted from certain species of red algae with a composition that consists of alternating 1,3-linked D-galactose-4-sulphated and 1,4-linked 3,6-anhydro-D-galactose monomers. The cryoprotective effects of polydextrose and κ - carrageenan may be attributed to the numerous hydroxyl groups available for hydrogen bonding with proteins, leading to increased protein hydration, reduced surface tension of water and decreased aggregation (denaturation) of myofibrillar pro-

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teins (Smolinska et al., 1995; Park et al., 1993). The aim of this research work was to investigate the cryoprotective effects of polydextrose and *k* - carrageenan by the use of differential thermal analysis (DTA).

MATERIAL AND METHODS

Surimi was prepared under laboratory conditions from the Adriatic pilchard (*Sardina philchardus*) by a modified industrial method (Lee, 1984). Samples of pilchard surimi were mixed with sodium tripolyphosphate (w_{pp} = 0.3%), *κ* - carrageenan (w_k = 0.5%) and polydextrose (w_p = 0-10%).

Chemical composition of surimi was determined by the standard methods of analysis according to the AOAC procedure for fish and fish product before mixing with the added substances (AOAC, 1980). After mixing with the added substances, samples were packed in polyethylene bags and fast frozen in liquid nitrogen and stored at - 20 °C. Average storage time was one week before DTA experiments.

DTA apparatus was constructed in the laboratory (Kovačević and Kurtanjek, 1993) and used for measurement of initial freezing point T_i. Thermocouples were made from Alumel-Chromel wire (0.07 mm diameter). The thermocouples were calibrated using a standard platinum resistance thermometer, Pt-100 at a temperature ranged -30 to 25 °C. The instruments were interfaced with a standard PC and a sampling rate of 3.5 kHz was used. All data were prefiltered with at +/-3σ rule for noise rejection prior to data analysis. From statistical analysis of the measurement signal, the calibration error of 50 mK and sensitivity of 10 mK were estimated. An aqueous solution of $CaCl_2$, w($CaCl_2$) = 30%, was used as reference substance for DTA measurement. This solution has water content and thermal properties almost identical to those of the pilchard, and what is even more important there is no change in the temperature interval of the DTA procedure (from -25°C to 5°C), as it freezes at the temperature of - 41°C.

Table 1. Basic chemical composition of pilchard surimi

	Water (%)	Proteins (%)	Fat (%)	Ash (%)
Mass fraction w / %	79,05	17,56	2,26	1,09

Table 2. Values (T_i) of samples of pilchard surimi mixed with 0.5% *κ* - carrageenan and different mass fractions of polydextrose

w polydextrose (%)	T_i / ºC	
	Experimental	Linear regression
0	-1,86	-1,73
1	-1,97	-1,81
2	-2,01	-1,89
3	-1,92	-1,98
4	-1,98	-2,06
5	-1,61	-2,14
6	-1,87	-2,22
7	-2,11	-2,30
8	-2,65	-2,38
9	-2,57	-2,47
10	-2,75	-2,55

RESULTS AND DISCUSSION

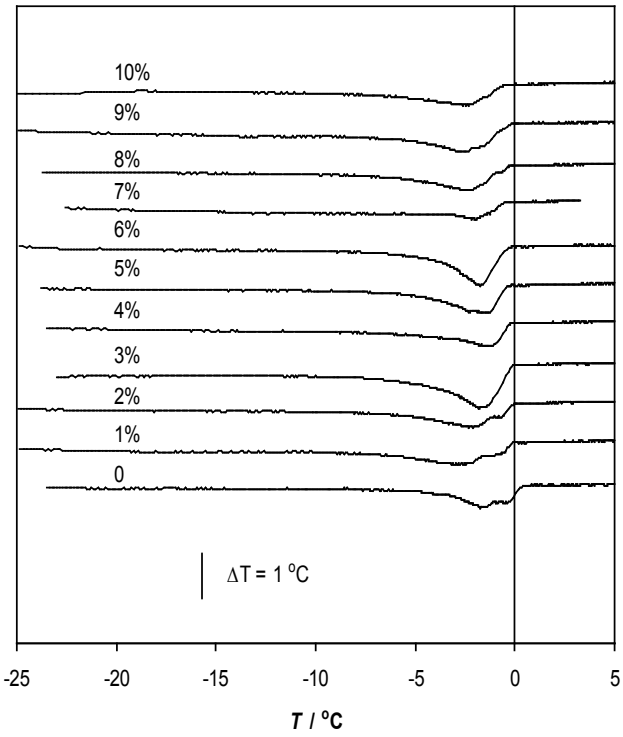
Basic chemical composition of pilchard surimi is presented in Table 1. DTA included 11 samples of pilchard surimi in the temperature range from -25 to 5ºC. Results of DTA are presented in Fig. 1. The DTA curves have a low level of measurement noise, which is a result of statistical data filtering and rejection of outliers by +/-3σ rule, as well as high frequency of data sampling. Drift from the base line at a the temperature ranged from 0 to 0.2°C occurred due to difference of thermal properties of samples and the reference substance. The peak points were read off as the initial freezing points from DTA diagrams. Table 2 presents the initial freezing points (T_i) of samples of pilchard surimi mixed with sodium polyphosphate (w_{pp} = 0.3%), *κ* - carrageenan (w_k = 0.5%) and polydextrose (w_p = 0-10%). Each DTA diagram of the initial freezing point is corrected only for constant error of + 0.1235355 ºC being determined from calibration with distilled water and entered into computer program for DTA monitoring for correction of the position of DTA curve peak.

The parameters of the regression equation were determined by the method of linear correlation of T_i with mass fraction of the polydextrose:

$$T_i = -1.73 + 0.082 w_p \qquad /1/$$

with standard error e(T)= 0.22 and coefficient of determination R^2 = 0.62. The highest cryoscopic decrease of the initial freezing temperature T_i was found in samples of pilchard surimi with the addition of κ-carrageenan (w = 0.5%) and a 10% of polydextrose. Experimental T_i values were compared with the initial freezing points, calculated with the Pham model (Pham, 1996):

Figure 1. DTA curves of pilchard surimi with 0.5% κ-carrageenan as a function of w (%) of polydextrose ΔT is temperature difference between sample and reference substance



$$T_i = -4.66 w_o / w_w - 46.4 w_a / w_w \qquad /2/$$

where w_o is the mass fraction of other components, w_w the mass fraction of water and w_a the mass fraction of ash.

Deviation of dependencies of the experimental values (Figure 2) of the initial freezing points T_i of samples of pilchard surimi and T_i values calculated with Pham model support the assumption that polydextrose acts in accordance with the cryoprotective mechanism and interacts with surimi myofibrillar proteins. Therefore, it increases the amount of bound water and decreases the initial freezing point T_i (Sych et al., 1995; Wang and Kolbe, 1991). Figure 3 presents the comparison of the initial freezing points T_i of surimi samples with the results for pilchard surimi with the addition of 0.5% κ-carrageenan and different mass fractions of polydextrose. These findings support the conclusion that κ-carrageenan also decreases the initial freezing point T_i of pilchard surimi, and thus also acts as cryoprotectant (Lenardić, 2006; Chen and Zhang, 2006).

Comparison of dependencies of T_i for pilchard surimi with 0.5% κ-carrageenan and water solution of polydextrose on mass fraction of polydextrose calculated on total mass of water is presented in Fig. 4. Deviations of initial freezing points T_i approve that polydextrose acts in accor-

Figure 2. Initial freezing points (T_i) of pilchard surimi mixed with polyphosphate (w_{pp} = 0.3%), κ-carrageenan (w = 0.5%) as a functions of mass fraction (w) polydextrose

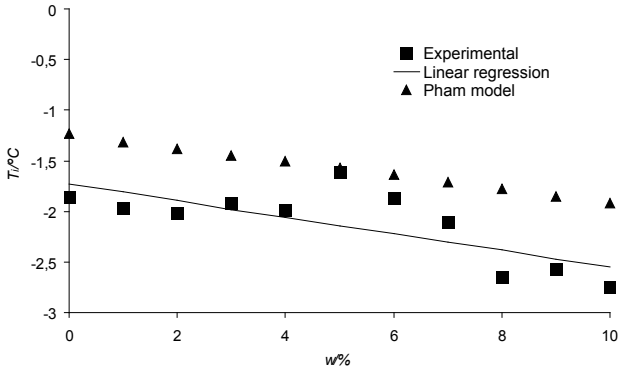


Figure 3. Initial freezing point (T_i) of pilchard surimi and pilchard surimi with 0.5% κ-carrageenan as a functions of mass fraction (w) of polydextrose

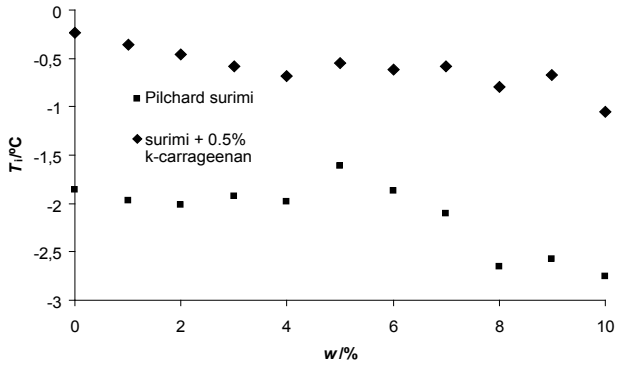
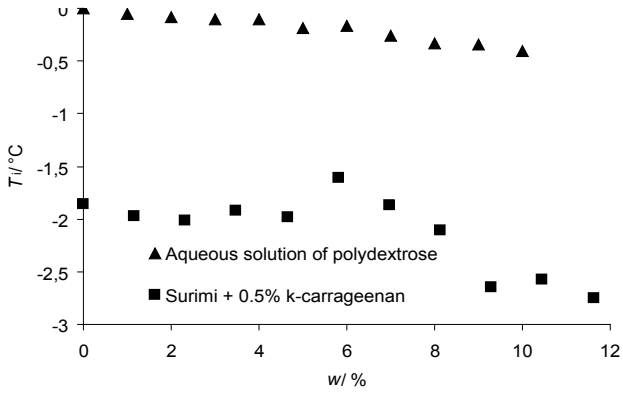


Figure 4. Comparison of dependencies T_i for pichard surimi with 0.5% κ-carrageenan and water solution of polydextrose on mass fraction (w) of polydextrose calculated on total mass of water



dance with the cryoprotecting mechanism and interacts with protein in surimi.

CONCLUSION

Freezing point depression of pilchard surimi with 0.5% κ-carrageenan is a linear function of the increased mass fraction of polydextrose. Deviations of experimental value for initial freezing points T_i, and results by the Pham model approve that polydextrose acts in accordance with the cryoprotecting mechanism and interacts with protein in pilchard surimi. The T_i values for samples of pilchard surimi and pilchard surimi 0.5% κ-carrageenan as a function of the mass fraction of polydextrose show deviations. It can be concluded that κ-carrageenan also interact with chicken surimi proteins and lowers T_i. The T_i values for samples of pilchard surimi with 0.5% κ-carrageenan and water solution of polydextrose as a function of the mass fraction of polydextrose calculated on the total mass of water were different for all the samples. The results support the assumption that polydextrose interacts with the protein in pilchard surimi by increasing the mass fraction of bound water and lowering the T_i.

ZUSAMMENFASSUNG

KRIPROTEKTO-WIRKUNG DER POLIDEXTROSE AUF SURIMISARDINEN

Durch die differenziale thermische Analyse (DTA) wurde die Anfangstemperatur des Gefrierens T_i der Surimisardinenmuster bestimmt, die mit Iskaragen_(w=0,5 %) und in verschiedenen Massenverhältnissen mit Polidextrose (w=1 – 10%) vermischt waren. Die Verbundenheit der Messinstrumente mit dem Computer ermöglichte eine unmittelbare on line Beobachtung des Abtauenprozesses von Mustern mit großer Empfindlichkeit der Temperaturmessung (10mK), die Musterungfrequenz (3,5 kHz) und die statische Filtration der gemessten Temperatur- und Zeitwerte (Regel ±3σ), sowie einfache Bearbeitung und graphische Interpretation der Angaben. Der Massenanteil von Wasser in den Surimisardinenmustern betrug vor der Mischung mit zusätzlichen Stoffen 79,05 %. Die Anfangstemperatur des Gefrierens von Surimisardinenmustern wurde aus der DTA Krümmung bestimmt. Durch die lineare Regression wurden die funktionale Abhängigkeit des Massenanteils der zugefügten Stoffe w und die Anfangstemperatur T_i bestimmt. Für alle Muster wurden die Determinationskoeffizienten bestimmt, die für die Surimisardinenmuster vermischt mit Iskaragen und in verschiedenen Massenverhältnissen mit Polidextrose R^2 = 0,62 betrugen. Die größte krioskopische Verminderung der Anfangstemperatur des Gefrierens zeigen die Surimisardinenmuster mit Zusatz von k-Karagen (w=0,5%) und 10% Polidextrose und sie beträgt –2,75° C. Die Experimentalresultate wurden mit den literarischen Angaben verglichen.

***Schlüsselwörter**: Anfangstemperatur des Gefrierens, DTA, Surimisardinen, Polidextrose, k-Karagen*

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