CRYOPROTECTIVE EFFECTS OF POLYDEXTROSE AND K-CARRAGEENAN ON PILCHARD SURIMI

Krešimir Mastanjević, Dragan Kovačević, Kristina Suman, Mirjana Lenardić

The Faculty of Food Technology, University J. J. Strossmayer Osijek, Department of Food Technology, Kuhačeva 18, 31 000 Osijek

SUMMARY

Initial freezing points (T_i) of surimi samples prepared from Sardina pilchardus 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 ºC. 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-
teins (Smolinska et al., 1995; Park et al., 1993). The aim of this research work was to investigate the cryoprotective effects of polydextrose and κ-carrageenan by the use of differential thermal analysis (DTA).

**MATERIAL AND METHODS**

Surimi was prepared under laboratory conditions from the Adriatic pilchard (*Sardina pilchardus*) by a modified industrial method (Lee, 1984). Samples of pilchard surimi were mixed with sodium tripolyphosphate (*w*<sub>pp</sub> = 0.3%), κ-carrageenan (*w*<sub>k</sub> = 0.5%) and polydextrose (*w*<sub>p</sub> = 0-10%).

Chemical composition of surimi was determined by the standard methods of analysis according to the AOAC procedure for fish and fish products 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<sub>i</sub>*. 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 range -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 pre-filtered with an +/-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 CaCl₂, *w*(CaCl₂) = 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.

**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 5°C. 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<sub>i</sub>*) of samples of pilchard surimi mixed with sodium polyphosphate (*w*<sub>pp</sub> = 0.3%), κ-carrageenan (*w*<sub>k</sub> = 0.5%) and polydextrose (*w*<sub>p</sub> = 0-10%). Each DTA diagram of the initial freezing point is corrected only for constant error of +0.1235355°C 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<sub>i</sub>* with mass fraction of the polydextrose:

\[
T_i = -1.73 + 0.082 w_p
\]

with standard error e(*T*)= 0.22 and coefficient of determination *R<sup>2</sup>* = 0.62. The highest cryoscopic decrease of the initial freezing temperature *T<sub>i</sub>* was found in samples of pilchard surimi with the addition of κ-carrageenan (*w* = 0.5%) and a 10% of polydextrose. Experimental *T<sub>i</sub>* values were compared with the initial freezing points, calculated with the Pham model (Pham, 1996):
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\[ T_i = \frac{-4.66w_o - 46.4w_w}{w_a} \]

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 \( w \) 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-

\[ \Delta T = 1 \, ^\circ C \]

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

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 pilchard 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 as a function of the 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 the freezing point.

It can be concluded that κ-carrageenan also interact with protein in pilchard surimi by increasing the mass fraction of bound water and lowering the freezing point $T_i$.

REFERENCES

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