THE EFFECT OF HYDROCOLLOID MIXTURES ON FROZEN PORK PROPERTIES

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The effect of three mixtures of hydrocolloids containing 1.5% protein isolate from cattle blood plasma AMP 600N and 0.2% carrageen E407, 1.5% protein isolate from cattle blood plasma AMP 600N and 0.4% carrageen E407, 1.5% protein isolate from cattle blood plasma AMP 600N and 0.4% satalginate S550, on the functional properties, the amount of frozen water and lipid oxidation in minced pork, stored at a temperature of -25°C for 135 days, was studied. It was proved that the mixture of 1.5% protein isolate from cattle blood plasma AMP 600N and 0.2% carrageen E407 counteracted the reduction of protein solubility to the largest extent, while the addition of the mixture of 1.5% protein isolate from cattle blood plasma AMP 600N and 0.2% carrageen E407 counteracted the reduction of protein solubility to the largest extent, while the addition of the mixture of 1.5% protein isolate from cattle blood plasma AMP 600N and 0.4% satalginate S550 stabilised water absorption of the tested meat at an initial level. All applied hydrocolloid mixtures reduced significantly the amount of frozen water in the analysed meat but did not affect the nature and the range of oxidative changes in lipids.

INTRODUCTION

Freezing is a known and generally accepted method for the preservation of raw materials and food products, used irrespective of their state of aggregation and geometrical form. The main advantage of this method is a prolonged preservation of the original composition and nutritive value of a product being preserved. A negative result of meat freezing is the change of physicochemical properties of myofibrilar proteins. The myofibrilar protein solubility [Park & Lanier, 1987 a, b; Sych & Lacroix, 1990 a,b], water absorption, the ability to emulsify fat and thermal stability of the formed muscle tissue-oil emulsions [Skrabka-Błotnicka, 1988] are deteriorated. As a consequence, the technological suitability of meat declines. Numerous researches proved that these negative changes can be limited by applying quick and ultra-quick freezing, ensuring stable temperature of frozen storage, using contour packing and by adding protective substances called cryoprotectants [Dziomdziora & Krala, 2000].

The best cryoprotective properties have these compounds that contain at least one of the three main functional groups, *i.e.* -COOH, -OH or -OPO₃H₂ and more than one completing functional group: -NH₂, -SH, -SO₃H [Dziomdziora & Krala, 1998]. Among many organic compounds that satisfy this requirement, so far only natural (sucrose, glucose) and synthetic saccharides (Polydextrose®), modified starch, modified cellulose and polyhydric alcohols, *e.g.* sorbitol, were used in practice. Studies on cryoprotection were concentrated mainly on the elimination of negative results of the freezing of myofibrilar protein isolates and fish and poultry surimi [Park & Lanier, 1988; Park & Lanier, 1993; McDonald & Lanier, 1991; Kijowski & Richardson, 1996]. It was confirmed that the protective effect occurred only when sucrose, glucose, Polydextrose® and sorbitol were added either at the concentration of 6-8% or in equilibrium mixtures, e.g. 4% sucrose + 4% sorbitol. The use of so high concentrations of cryoprotectants causes a change in the original composition of the preserved product and its organoleptic properties [Tomaniak & Tyszkiewicz, 1997]. In literature there are no accounts on the applicability of cryoprotectants to preserve the properties of frozen meat of slaughter animals, including functional properties. Sucrose, the cheapest and most often applied cryoprotectant for surimi preservation, causes sweet taste and deteriorates the colour of this product. Also for these reasons sucrose cannot be used as a cryoprotectant for frozen meat of slaughter animals. It can be replaced by Polydextrose® or sorbitol. At the present state of the art, it cannot be decided which of the cryoprotectants tested so far is the best to protect meat against freezing changes. Research carried out recently by the authors of this paper led to the conclusion that none of the known cryoprotectants (Polydextrose®, Soritol, saccharose, karagene) stabilised all functional properties of frozen meat [Dziomdziora & Krala, 2000]. To fully protect meat against negative results of freezing, it seems necessary to add a mixture of several cryoprotectants. Until now, the applicability of hydrocolloids for this purpose has not been analysed although, due to their structure and properties, they satisfy the theoretical requirements of cryoprotectants. Moreover, now these substances have become popular additives to meat products. Carrageens, alginates, animal and vegetable protein isolates can be used at small concentrations ranging from 0.1 to 2%[Tyszkiewicz, 1992; Adamczyk et al., 2001]. Recently, it has been reported that hydrocolloids used in mixtures can be more efficient than when applied separately [Gustaw & Mleko, 2001].

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The aim of this study was to determine the effect of the mixture of hydrocolloids on selected functional properties and lipid oxidation in minced pork during frozen storage.

MATERIALS AND METHODS

The material to be tested was fresh pork (neck) from industrial slaughter, taken 24 h after the moment of slaughter. To obtain homogeneous samples, the meat was minced twice at a temperature of 4°C using a Zelmer 686,5 electric mincer with mesh holes of diameter $\Phi=2$ mm. After mincing and thoroughout mixing, the meat was divided into four samples for analysis. The mixtures of powdered hydrocolloids listed in Table 1 were added to particular samples. To simplify the notation, in the discussion of results, a protein isolate from cattle blood plasma (AMP 600N) is called briefly the protein isolate. The symbols of samples given in Table 1 were used in the description of Tables and Figures.

TABLE 1. List of additives used in pork and symbols of samples.

| No. | Concentration and type of applied additives | Sample symbol |
|-----|--|------------------|
| 1 | Meat with no additives | РК |
| 2 | 0.4% satalginate \$550 +1.5% protein | |
| | isolate from cattle blood plasma (AMP 600N) | 0.4S |
| 3 | 0.2% carrageen (E407) +1.5% protein | |
| | isolate from cattle blood plasma (AMP 600N) | 0.2K |
| 4 | 0.4% carrageen (E407) +1.5% protein | |
| | isolate from cattle blood plasma (AMP 600N) | 0.4K |

The samples were packed into bags made of two-layer PA/PE film. All samples were frozen to a temperature of -25°C and stored at this temperature for 135 days. To determine the changes in the properties of tested meat, the samples were analysed immediately before freezing and after various storage periods. The analyses included: (i) soluble protein content - the proteins were extracted by Dyer's method, the content of proteins in the extract was determined by Lawry's method [Krełowska-Kułas, 1993]; (ii) the amount of frozen-out water - by calorimetric method [Krala, 1994]; (iii) the water holding capacity (WHC) - by Grau-Hamm filter paper-pressure method modified by Krala [Krala, 1995]; (iv) the amount of secondary products of lipid oxidation - by TBA test [Krełowska-Kułas, 1993]; (v) peroxide content - Lea number [Krełowska-Kułas, 1993].

In each storage period, 5 samples from each experimental variant were analysed. Arithmetic means and standard deviations were calculated. The values of standard deviations were marked in figures representing experimental results. The significance of differences between analytical results in particular storage periods was estimated using variance analysis (F-test) and Student's t-test, at the significance level of 0.05.

RESULTS AND DISCUSSION

Changes in protein properties that occurred in frozen meat are most frequently evaluated on the basis of solubility in the solutions at increased ionic strength. This index well represents the native state of proteins and reveals high

interdependence with changes in the other functional features [Stangierski, 1999]. After the storage, in the analysed meat without additives the protein solubility decreased by 27%. When the protein isolate mixed with carrageen and satalginate was added to the tested meat, a significant growth of soluble protein content was reported as compared to the control sample (Figure 1). At the end of the whole period of frozen storage of the meat with the tested additives, a decrease in protein solubility was reported depending on the additive concentration. In the samples with the addition of 1.5% protein isolate and 0.4% satalginate, the content of soluble proteins decreased by 16%. In the least degree (by 16%), the soluble protein content decreased in the frozen meat with 1.5% protein isolate and 0.2% carrageen. It means that the latter mixture of hydrocolloids best stabilises the content of soluble proteins. It was shown that growth of the carrageen concentration to 0.4% caused a decrease in soluble protein content. It can be presumed therefore that there is some optimum concentration of carrageen added to meat which, when exceeded, causes a result opposite to the desired one, probably because of too strong dewatering of proteins, and as a consequence, deterioration of their physicochemical properties. A positive effect of carrageen on the soluble protein content in frozen meat confirms the hypothesis of antidenaturation properties of these compounds. Kołakowski and Winecki [1996] proved that the antidenaturation activity of carrageen is related to a better exposition of anionic groups of this hydrocolloid, and consequently an increase in hydration of muscle proteins. This leads to an increase in water absorption in the muscles and reduces hydration of proteins during freezing and frozen storage.



FIGURE 1. Changes of soluble protein content in frozen pork during storage at -25°C.

All cryoprotective mixtures used in the discussed experiments cause a decreased in the amount of frozen water in meat (Table 2). The mixture that induces the highest reduction consisted of 1.5% protein isolate and 0.4% satalginate. In these samples the amount of frozen water was nearly 8% lower than in the control sample. A significant decrease in the frozen water in meat is a result

TABLE 2. The effect of cryoprotectives on the amount of frozen free water in pork at -25°C

| Frozen-out water $\omega \pm SD [\%]$ | | | | | | |
|---------------------------------------|----------------|----------|----------|--|--|--|
| РК | 0.4S | 0.2K | 0.4K | | | |
| 99.7±2.2 | 92.1 ± 2.5 | 95.4±1.7 | 93.7±2.3 | | | |

of a strong hydrocolloid-water interaction. This leads to a shift of the ice front-concentrated solution equilibrium towards the substance that is not frozen.

The results of the analysis of water holding capacity (WHC) in meat with the addition of hydrocolloids are illustrated in Table 3. The action of tested cryoprotectants on the reduction of drip forced from the tested meat was different and decreased with the time of frozen storage. Investigations proved that with an increase in the concentration of analysed additives in meat there is a statistically significant increase in WHC in the frozen meat. The mixture of 1.5% protein isolate with 0.4% satalginate appeared to be the most efficient in stabilising the intrinsic water absorption. For the entire period of frozen storage, WHC of this sample was kept at the initial level and was significantly higher than in other samples. The results obtained suggest that satalginate is more efficient than carrageen in stabilising the WHC of meat. When analysing changes in the water absorption in meat with the addition of hydrocolloids, Lian et al. [2000] suggested that satalginate and carrageen prevent interactions of muscle fibres due to their electrostatic repulsion and chelate formation of

TABLE 3. Changes of water holding capacity (WHC) in frozen pork during storage at -25°C.

| Time [days] | WHC ± SD [cm ³ drip/100 g meat] | | | | |
|----------------|---|-----------------|-----------------|-----------------|--|
| | PK | 0.4 S | 0.2 K | 0.4 K | |
| 0 | 0.63 ± 0.02 | 0.00 ± 0.00 | 0.00 ± 0.00 | 0.00 ± 0.00 | |
| 34 | 0.75 ± 0.02 | 0.00 ± 0.00 | 0.77 ± 0.03 | 0.59 ± 0.03 | |
| 74 | 0.82 ± 0.07 | 0.00 ± 0.00 | 0.95 ± 0.03 | 0.80 ± 0.04 | |
| 106 | 1.04 ± 0.10 | 0.00 ± 0.00 | 1.00 ± 0.07 | 0.96 ± 0.05 | |
| 135 | 1.35 ± 0.10 | 0.00 ± 0.00 | 1.10 ± 0.06 | 1.20 ± 0.05 | |



Figure 2. Changes of TBA index in frozen pork during storage at -25°C.

calcium ions. As explained by these authors, hydrocolloids fill up the space between fibres forming gel matrix. In this way, the thawing drip is reduced and the meat ability to keep intrinsic water is increased.

The TBA index is one of the most reliable evaluation factors of oxidative changes of lipids in frozen meat. The results of the performed tests are shown in Figure 2. In all samples, a slight increase in the TBA index was observed no sooner than after 106 days of frozen storage. A statistical analysis showed that the change was not significant in relation to initial values. The slight oxidative changes in lipids were confirmed by the results of investigations of the Lea number (Table 4). Values of this parameter changed only at the end of the frozen storage period, irrespective of cryoprotectants added. Hence, it can be stated that none of the tested hydrocolloids has effect on the oxidative changes of lipids in frozen pork.

TABLE 4. Changes of the Lea number in frozen pork during storage at -25°C.

| Time [days] | Lea number [cm ³ 0.002N Na ₂ S ₂ O ₃ /g fat] | | | | |
|----------------|---|-------------------|-------------------|-------------------|--|
| | PK | 0.4 S | 0.2 K | 0.4 K | |
| 0 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | |
| 34 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | |
| 74 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | |
| 106 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | 0.005 ± 0.000 | |
| 135 | 0.240 ± 0.030 | 0.210 ± 0.050 | 0.230 ± 0.010 | 0.220 ± 0.010 | |

CONCLUSIONS

1. During frozen storage of minced pork a decrease in protein solubility was observed, depending on the type of cryoprotectants added. The best cryoprotective properties were reported for the mixtures of hydrocolloids containing 1.5% protein isolate from cattle blood plasma AMP 600N and 0.2% carrageen and 1.5% protein isolate from cattle blood plasma AMP 600N and 0.4% satalginate S550.

2. All analysed mixtures of hydrocolloids decreased significantly the amount of frozen-out water in pork.

3. The ability to retain water in the tested meat increased with an increase in the per cent of carrageen and satalginate in hydrocolloid mixtures. The most efficient in this respect appeared to be the mixtures of satalginate and protein isolate from cattle blood.

4. The tested hydrocolloid mixtures did not affect oxidative changes of lipids in frozen pork.

5. The analysed mixtures of hydrocolloids can be used in frozen preservation of minced pork.

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REFERENCES

1. Adamczyk L., Słowiński M., Plewicka M., Wpływ wybranych dodatków funkcjonalnych na jakość niskotłuszczowych kiełbas drobnorozdrobnionych. Mięso i Wędliny, 2001, 2, 36–44 (in Polish).

- Dziomdziora M., Krala L., Krioprotekcja białek mięśniowych. Chłodnictwo, 1998, 33, 2, 38–41 (in Polish).
- 3. Dziomdziora M., Krala L., The effect of selected cryoprotectants on the properties of frozen pork. Pol. J. Food Nutr. Sci., 2000, 9/50, 1, pp. 47–50.
- Gustaw W., Mleko S., Synergistyczne interakcje występujące pomiędzy polisacharydami w ich mieszaninach. Żywność, Technologia, Jakość, 2001, 3, 28, 5–12 (in Polish).
- Kijowski J., Richardson R., The effect of cryoprotectants during freezing or freeze drying upon properties of washed mechanically recovered broiler meat. Inter. J. Food Sci. Technol. 1996, 31, 45–54.
- Kołakowski E., Winecki M., Stabilizujący wpływ iota-karagenu na właściwości funkcjonalne rozdrobnionego mięsa leszcza podczas zamrażalniczego przechowywania, 1996, *In*: Proceedings of XXVII Sesja Naukowa KTiChŻ. PAN (in Polish).
- Krala L., Wpływ warunków wykonywania pomiarów na wynik oznaczania wodochłonności mięsa bydlęcego. Zeszyty Naukowe Politechniki Łódzkiej, 1995, nr 631. Technologia i Chemia Spożywcza, z. 49, 133–144 (in Polish).
- Krala L., Pomiar ilości wymrożonej wody. 1994, *In*: Technologia Chłodnictwa Żywności. Procesy i ich kontrola. (ed. S. Michałowski). Wydawnictwo Politechniki Łódzkiej, Łódź, 67–84 (in Polish).
- Krełowska-Kułas M., 1993, Badanie jakości produktów spożywczych. Państwowe Wydawnictwo Ekonomiczne, Warszawa, 33–36 (in Polish).
- McDonald G.A Lanier T.C., Carbohydrates as cryoprotectants for meat and surimi. Food Technol., 1991, 45, 3, 150–160.
- 11. Lian P.Z, Lee C.M., Hufnagel L., Physicochemical properties of frozen red hake meat as affected by cryoprotective ingredients. J. Food Sci., 2000, 65, 7, 1117.
- Park J.W., Lanier T.C., Effect of cryoprotectants in minimizing physicochemical changes of bovine natural actomyosin during frozen storage. J. Food Biochem., 1987 a, 11, 143–161.

- 13. Park J.W., Lanier T.C., Combined effect of phosphates and sugar or polyol on protein stabilization of fish myofibrils. J. Food Sci., 1987 b, 52, 6, 1509–1513.
- 14. Park J.W., Lanier T.C., Cryostabilization of functional properties of pre-rigor and post-rigor beef by dextrose polymer and/or phosphates. J. Food Sci., 1993, 58, 3, 467–472.
- Park J.W., Lanier T.C., Cryoprotective effect of sugar, polyols, and/or phosphates on Alaska Pollock surimi. J. Food Sci., 1988, 53, 1, 1–3.
- Skrabka-Błotnicka T., Zdolność wiązania wody przez mięśnie piersiowe kaczek przechowywanych w temperaturze -18°C i -2°C. Chłodnictwo, 1988, 23, 7, 15–17 (in Polish).
- Stangierski J., Wpływ wybranych stabilizatorów białek na jakość suszonego sublimacyjnie przemywanego mięsa drobiu odzyskanego mechanicznie. Żywność, Technologia, Jakość, 1999, 2, 19, 26–38 (in Polish).
- Sych J., Lacroix C., Cryoprotective effect of lactitol, palatinit and Polydextrose[®] on cod-surimi proteins during frozen storage. J. Food Sci., 1990 a, 55, 2, 356–360.
- Sych J., Lacroix C., Cryoprotective effect of some materials on cod-surimi proteins during frozen storage. J. Food Sci., 1990 b, 55, 5, 1222–1227.
- 20. Tyszkiewicz J., Zamienniki tłuszczu w przetwórstwie mięsa. Gospodarka Mięsna, 1992, 11, 12 (in Polish).
- Tomaniak A., Tyszkiewicz J., Smakowe uwarunkowania zastosowania krioprotektantów w mięsie, 1997, *In:* Proceedings of XXVIII Sesja Naukowa KTiChŻ PAN, 1997, Gdańsk, 8 (in Polish).

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WPŁYW DODATKU MIESZANIN HYDROKOLOIDÓW NA WŁAŚCIWOŚCI MROŻONEGO MIĘSA WIEPRZOWEGO

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Badano wpływ dodatku trzech mieszanin hydrokoloidów o składzie: 1,5% izolat białek z plazmy krwi bydlęcej AMP 600N i 0,2% karagen E407; 1,5% izolat białek z plazmy krwi bydlęcej AMP 600N i 0,4% karagen E407; 1,5% izolat białek z plazmy krwi bydlęcej AMP 600N i 0,4% satalginian S550, na właściwości funkcjonalne, ilość wymrożonej wody oraz oksydację lipidów (tab. 4) w mielonym mięsie wieprzowym, przechowywanym w temperaturze -25°C przez okres 135 dni. Wykazano, iż mieszanina 1,5% izolatu białek z plazmy krwi bydlęcej AMP 600N i 0,2% karagenu E407 w największym stopniu przeciwdziała obniżaniu się rozpuszczalności białek (rys. 1), natomiast dodatek mieszaniny 1,5% izolatu białek z plazmy krwi bydlęcej AMP 600N i 0,4% satalginianu S550 stabilizuje wodochłonności badanego mięsa na początkowym poziomie (tab. 3). Wszystkie zastosowane mieszaniny hydrokoloidów znacząco obniżają ilość wymrożonej wody w analizowanym mięsie (tab. 2), lecz nie wpływają na charakter i zakres zmian oksydacyjnych lipidów (rys. 2).