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THE EFFECT OF STORAGE ON PHYSICOCHEMICAL PROPERTIES OF SPRAY-DRIED MILK, EGG AND MILK-EGG MIXTURE

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Abstract. The aim of this work was to obtain a new spray-dried milk-egg mixture and to compare its physicochemical properties with the properties of whole milk powder and egg powder. The powders prepared were packaged in bags under air and vacuum and stored for 24 months. During storage all of the properties assayed (lightness, hydroxymethylfurfural, Maillard browning intensity, thiobarbituric acid reactive substances, solubility index, pH) deteriorated. The addition of milk to egg before drying improved the solubility of egg powder. Solubility of milk powder was higher than 2 cm^3 in the twelfth month of storage. For this reason the powders retained their best qualities till the sixth month of storage. The kind of packaging had an influence on the quality of the products (vacuum packaging delayed the deterioration of powders).

Keywords: powdered food, milk-egg mixture, storage

INTRODUCTION

Food concentrates are used in different kinds of food industry. They are produced by evaporation of water from raw material by different methods, for example spray-drying, freeze-drying, convection or others. Concentrated milk has a higher osmotic pressure compared to the raw material. Powdered concentrates are characterised by low water activity and that is why their shelf-life is so long. However, even in such highly dehydrated foods there can take place reactions like lipid oxidation or interactions of proteins and carbohydrates. Those changes cause the degradation of physicochemical and sensory quality of powders (Kim *et al.* 2009, Koç *et al.* 2012, Semeniuc *et al.* 2008, Thomas *et al*. 2004). For the inhibition of the changes in powders occurring during storage, they are packaged in vacuum or inert gas environment (Han 2013, Lloyd *et al.* 2004).

Whole milk and egg are used in the food technology as raw materials or dried components. Both of them may be present in cakes, ice-creams, omelettes, powder deserts (Asgar and Abbas 2012). The egg powder is characterised by low solubility, wetting and flowability causing the dosing problems. For the improvement of egg powder properties, raw milk and egg were mixed and spray-dried. The milk-egg powder obtained in that way can be used as a semi-product for the preparation of pancakes or other cakes.

The aim of this study was to obtain a new milk-egg powder and to compare its physicochemical properties with those of whole milk powder and egg powder. The powders were stored in poly(ethylene terephthalate)/polyethylene bags for 24 months in air and vacuum environment.

MATERIAL AND METHODS

To obtain a milk-egg mixture, 100 litres of whole liquid milk and 800 eggs were combined. One litre of fresh liquid milk to 8 eggs is a typical ratio in pancake batter (Berger *et al.* 1997). The volume milk-egg ratio was 1 : 0.40. Characterisation of raw materials is presented in Table 1. The procedure of milk and egg mixture powder production is shown in Figure 1. Samples of whole milk powder and egg powder were prepared according to the same procedure. “Fat content in the tested milk powder was 26.4%, in egg powder 42.9% and in mix powder – 34.8%. The content of water in analysed products was 2.4%, 4.0% and 3.2%, respectively” (Chudy *et al.* 2015). The powders were stored without light at 20°C with a maximum humidity of 75%. Packaging bags were made of polyester and polyethylene film. The thickness of the polyester was 12 μm and polyethylene 60 μm. The layer in contact with the product was made of polyethylene. The weight of the film with a width of 330mm was 24.4 g m^{-1}. The laminate had water vapour permeability of 12 g m^{-2} 24h and oxygen permeability of 73 cm^3 m^{-2} 24 h 0.1 MPa. The powders were packaged under air and vacuum conditions.

Analyses were made after the production and every 6 months for two years of storage.

Table 1. Characterisation of raw materials used for production of analysed powders

Factor / Raw material	Dry matter (%)	pH	Lightness L*	Colour parameter a*	Colour parameter b*
Milk	12.00	6.61	88.74	–2.04	8.41
Egg	23.04	7.35	75.25	3.21	32.15
Milk + egg	15.57	7.03	80.56	0.05	21.35

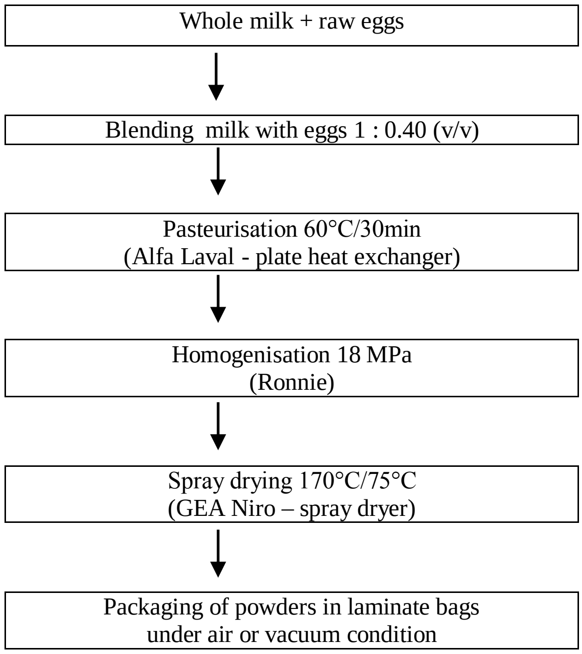

Fig. 1. Diagram of production of milk-egg powder

Reconstitution of powders

For the reconstitution of spray-dried samples 12.0 g of whole milk powder, 23.0 g of egg powder and 15.6 g of the mix powder were taken and supplemented with distilled water to 100 g. Thereby the reconstituted liquid products were similar dry matter to this given in Table 1. The powder and water ware stirred for 5 min. to obtain a homogeneous material. To that end, a Hobart Bowl Mixer Type CE100 (Peterborough, Ireland) was used.

Lightness and colour difference

The lightness of the powders was measured using X-Rite SP-60 spectrophotometer (Grandville, USA) with a 1 cm thickness of the layer and the D source of light. The data were performed in the CIELAB colour system where L* defines lightness. The lightness and other colour components: a* and b* were used to calculate the colour difference (the distance between 2 points in the colour area) according to the formula:

$$\Delta E=[\Delta L^2 + \Delta a^2+ \Delta b^2]^{1/2}$$

The relationship of the calculated difference to human perception can be divided as follows: < 0.2 not observable, 0.2-1 very slight, 1-3 slight, 3-6 average, > 6 large. Factor ΔE was calculated between powders stored 0 and 6 months, 6 and 12 months, 12 and 18 months, 18 and 24 months (CIE 2004).

Hydroxymethylfurfural content in whole milk powder

Total content of hydroxymethylfurfural (HMF) was determined in whole milk powder after reconstitution and heating at 100°C for 60 min following its acidification with an 0.3 N solution of oxalic acid. The cooled milk was supplemented with 40% trichloroacetic acid (TCA) and filtrated through Whatman N°42 blotting paper. The filtrate was treated with an 0.05 M solution of thiobarbituric acid (TBA) and incubated for 35 min at 40°C. The absorbance (A) was measured at 443 nm wavelength against a control sample using a Novaspec II spectrophotometer (Amersham Pharmacia Biotech, Athens, Greece) (Keeney and Bassette 1959). Egg and mix powder underwent denaturation in this test so HMF was determined only for milk power.

$$\text{total HMF } (\mu\text{mol dm}^{-3}) = [(A - 0.055)\cdot 87.5]$$

Maillard browning intensity

The Maillard browning intensity (MBI) determination was performed following the method described by Tsai and Hudson (1985), modified by Guardiola *et al.* (1995). To 0.8 g of powder 10 cm^3 10% (w/v) solution of trichloroacetic acid was added and homogenised by magnetic stirring for 10 min. The mixture was filtered, placed into 10 mL volumetric flask and diluted to the volume. The absorption was measured (to the reference sample) at 420 nm in Novaspec II spectrophotometer (Amersham Pharmacia Biotech, Athens, Greece).

Thiobarbituric acid reactive substances

The Thiobarbituric acid reactive substances (TBARS) were determined according to the method by Angulo *et al.* (1997), slightly modified. To 2 g of lipids extracted from analysed powders by chloroform:methanol (2:1, v/v) (Folch *et al.* 1957) 8 cm^3 of distilled water, 6 cm^3 0.6% (w/v) TBA in 0.25 M HCl and 3 cm^3 20% trichloroacetic acid were added. The tubes were shaken and heated at 100°C for 20 min. After cooling, the samples were centrifuged (3000 x g) for 10 min and diluted to volume 20 cm^3. TBARS were measured against a control sample spectrofluorophotometrically at 533 nm using a Novaspec II spectrophotometer (Amersham Pharmacia Biotech, Athens, Greece).

Solubility index

The solubility index is a volume, in millilitres, of sediment (insoluble residue) obtained when reconstituted products were centrifuged, under the conditions specified in International Standard ISO 8156:2005.

pH value

The pH value was measured in reconstituted powders using pH-meter CX-732 (Elmetron, Zabrze, Poland).

Amount of scorched particles in a powder

The amount of scorched particles in analysed powders was determined by comparison with the ADMI chart: Scorched Particle Standards for Dry Milk. The results were compared with the original ADMI standard chart. The comparison was visual. The standard chart is divided into a scale from A-D. If a sample is classified as being between two standards it is always set at the highest value (ADPI Bulletin 916).

Statistical analysis

Results given in the tables are averages from 9 measurements (3 replications from each production part). Data collected experimentally were analysed statistically using the Fisher test in the Statistica 6.0 software package.

RESULTS AND DISCUSSION

The changes of lightness of analysed powders are shown in Table 2. They could be caused by non-enzymatic browning reactions (Maillard reactions, lipid peroxidation, degradation of ascorbic acid or sugar-sugar caramelisation) (Davies and Labuza 1997). The reaction of amino group of lysine and carbonyl group of lactose is the main one in whole milk powder. Some products formed during non-enzymic reactions are stable, others turned further. Sugars like pentose or xylose undergo dehydration and, losing a water molecule, become furfural or hydroxymethylfurfural (HMF) (Jing and Kitts 2000, Makawi *et al*. 2009). The obtained results demonstrated the impact of the kind of powder, packaging system and storage time on L* colour component.

The content of HMF in analysed whole milk powder changed as follows (in brackets are the values for vacuum-packaged powders) 7.25 μmol dm^{-3}, 9.90 (9.24), 15.51 (14.53) 19.83 (18.28) and finally 23.94 (21.02). This compound is not desirable in food products and its toxicity and mutagenicity are still controversial (Abraham *et al*. 2011).

Table 2. Lightness (L), difference of colour (ΔE) and Maillard Browning Intensity (MBI) of whole milk powder, egg powder and mix powder during storage in air and vacuum for 24 months

Powder	Time	Lightness (L)		ΔE		MBI	
		A	V	A	V	A	V
Whole Milk powder	0	93.13	93.13	–	–	0.04aA*	0.04aA
	6	91.02	91.86	2.3	1.3	0.08bA	0.07abB
	12	90.66	91.92	0.7	0.2	0.12cA	0.08bB
	18	91.32	90.22	0.9	1.7	0.23dA	0.10cB
	24	94.12	93.94	4.1	4.5	0.30eA	0.16dB
Egg powder	0	86.27	86.27	–	–	0.26dA	0.26fA
	6	83.55	84.77	3.0	1.6	0.49gA	0.44hB
	12	82.31	83.06	1.3	1.8	0.64iA	0.50iB
	18	86.01	85.70	6.3	6.7	0.78jA	0.56jB
	24	85.94	85.56	10.0	4.3	0.89kA	0.60kB
Mix powder	0	89.81	89.81	–	–	0.08bA	0.08bcA
	6	88.32	88.70	2.4	1.9	0.26dA	0.20eB
	12	86.83	87.66	1.1	1.1	0.35fA	0.30gB
	18	89.88	88.87	8.0	0.8	0.47gA	0.44hB
	24	90.44	89.80	11.6	2.9	0.58hA	0.50iB

A – air package, V – vacuum package;
*****Different small letters in columns and different capital letters in rows indicate statistically significant difference at p = 0.05.

Maillard browning intensity (MBI) increased during storage in all analysed powders. The egg yolk usually contains 0.5% of free reducing sugars, like glucose. The interactions of glucose and proteins could be the main reason of deterioration of dried egg products during storage.

The other reason of darkening of analysed powders could be migration of free lipids and β-carotene on the surface of powder drops (Nielsen *et al*. 1997). The lipid oxidation of milk and egg powder widely described by Chudy *et al.* 2008 and Chudy *et al.* 2015 can also cause the formation of colour compounds.

At the end of the storage period lightening of analysed powders was observed. This effect could be explained by degradation of β-carotene during the oxidation process (Chavez-Servin *et al*. 2008, Guardiola *et al*. 1997). Vitamin A is stable under an inert atmosphere; however, it rapidly loses its activity when heated in the presence of oxygen (Lešková *et al*. 2006). Caboni *et al.* (2005) showed that the content of vitamin A and E decreased during storage of egg powder for 12 months at 20°C, by 40% and 25%, respectively.

The brightening of powders suggests far-reaching changes in fats. This is confirmed by the increase of TBARS values during storage (Tab. 3).

Table 3. TBARS, solubility index and pH of whole milk powder, egg powder and mix powder during storage in air and vacuum for 24 months

Powders	Time of storage (months)	TBARS		Solubility index (cm^3 of precipitate)		pH	
		A	V	A	V	A	V
Whole milk powder	0	0.02aA	0.02aA	0.1aA	0.1aB	6.73dA	6.73cA
	6	0.04aA	0.05aA	0.6bA	0.6bB	6.25bA	6.51bB
	12	0.07aA	0.06aA	3.1cA	2.2dB	6.23abA	6.40abB
	18	0.10abA	0.09abA	7.2dA	6.2fB	6.18abA	6.34aB
	24	0.28bA	0.24bA	12.4gA	11.1hB	6.14aA	6.31aB
Egg powder	0	0.07aA	0.07aA	3.2cA	3.2eA	9.27kA	9.27kA
	6	0.46bcA	0.46dA	10.5fA	8.5gB	8.55jB	8.83jA
	12	1.00dA	0.91eA	20.0hA	17.3iB	8.07iB	8.34iA
	18	1.36eA	1.07eB	27.3iA	25.1jB	7.83hB	8.13hA
	24	1.48efA	1.26efB	35.1jA	32.0kB	7.65gB	8.00hA
Mix powder	0	0.12abA	0.12cA	0.9bA	0.9bA	7.26gA	7.26fA
	6	0.55cA	0.51dA	3.1cA	1.2cB	7.03fA	7.11efA
	12	1.21deA	1.18eA	8.0eA	6.5fB	6.95efA	7.05eA
	18	1.32eA	1.28efA	12.2gA	10.2hB	6.85eA	7.03eB
	24	1.52fA	1.40fB	19.7hA	18.4iB	6.60cA	6.91deB

A – air package, V – vacuum package; *****Different small letters in columns and different capital letters in rows indicate statistically significant difference at $p = 0.05$.

The changes described above influenced also the solubility of powders. After production the solubility index of whole milk powder and mix powder were low and amounted to 0.1 cm^3 and 0.9 cm^3, respectively. The egg powder was characterised by a higher solubility index (3.2 cm^3). The solubility of milk and mix powder compared to the solubility of egg powder is better mainly due to the lower fat content, 16.5% and 8.1% respectively. The analysed whole milk powder stored for 6 months in both air and vacuum conditions had still good solubility (0.6 cm^3), but the solubility of egg and milk-egg powder decreased and their solubility index increased to 10.5 cm^3 and 3.1 cm^3, respectively. According to ADPI (American Dairy Products Institute), the solubility index of whole milk powder should not be higher than 2 cm^3. The solubility of good quality whole milk powder ranges from

96% to 99%. When production or storage conditions are inappropriate, the solubility of powder may decrease below 50%. The solubility index shows that analysed powders were characterised by good quality only for 6 months of storage. The decrease of solubility of powders which contain eggs could be connected with three reasons: content of reducing sugars, moisture of powder and temperature of storage. Removal of glucose from eggs before drying could delay the decrease of solubility and prevent undesirable conversion of powders during storage. The decrease of powder solubility could be caused by a two-step reaction-degradation of glucose and formation of insoluble compounds. Addition of some amino acids, like cysteine, glycine and alanine, effectively prevents losses of powders' solubility but does not cause any inhibition of browning reactions. Low solubility of egg powder can be also explained by the formation of a thin layer of wet particles on the phases border which makes the penetration of water into the particles of powder difficult.

The acidity of analysed powders increased during storage. The pH value of milk, egg and mixture powders amounted to 6.73, 9.27 and 7.26, respectively, immediately after production and decreased by 0.59, 1.62 and 0.66 after 24 months of storage in bags under air condition and by 0.40, 1.27 and 0.35 in bags in vacuum condition. Kind of powder, time and way of storage (air or vacuum) had a significant impact on the changes of pH. Increase of acidity of analysed powders could be caused by reaction of glucose with proteins and phospholipids. Amino groups are blocked in these reactions and the content of free acids is stable. Hydrolysis and formation of free fatty acids and fat oxidation process can cause an increase of acidity of powders.

No burned particles and contaminants were detected in all analysed powders. After filtration, filters were compliant to the standard A.

CONCLUSIONS

1. Examined characteristics, i.e. lightness, hydroxymethylfurfural, Maillard browning intensity, solubility index, pH in powder prepared from milk-egg mixture were intermediated between the factors for milk powder and egg powder (except thiobarbituric acid reactive substances).
2. Addition of milk to egg caused an increase of the solubility of prepared powder.
3. Kind of powder (milk, egg, milk-egg) had significant influence on all determined factors. The largest percentage differences between the first and last analysis were noted in MBI and solubility index for milk powder, in TRARS and pH in the egg powder (all in powders packaged in air environment).
4. Vacuum packaging delayed the deterioration of powders.

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WPŁYW PRZECHOWYWANIA NA CECHY FIZYKOCHEMICZNE MLEKA, JAJ I MIESZANKI MLECZNO-JAJOWEJ W PROSZKU

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S t r e s z c z e n i e . Celem pracy było wyprodukowanie nowych proszków mleczno-jajowych i porównanie ich właściwości fizykochemicznych z właściwościami pełnego mleka i jaja w proszku. Proszki zostały zapakowanie w woreczki z tworzywa sztucznego w otoczeniu powietrza oraz próżni i poddane przechowywaniu przez okres 24 miesięcy. Podczas przechowywania wszystkie oznaczane cechy uległy pogorszeniu (jasność, hydroksymettylofurfural, intensywno brązowienia, związki reagujące z kwasem tiobarbiturowym, indeks rozpuszczalności, pH). Dodatek mleka do jaj spowodował polepszenie rozpuszczalności proszku jajowego. W 12 miesiącu przechowywania rozpuszczalność mleka w proszku była wyższa niż zalecenia (tj. >2 cm^3). Z uwagi na ten fakt stwierdzono, że proszki zachowały swoje najlepsze cechy do 6 miesiąca przechowywania. Sposób pakowania miał statystycznie istotny wpływ na badane właściwości fizykochemiczne (pakowanie próżniowe opóźniało proces starzenia się proszków).

S ł o w a k l u c z o w e : koncentraty w proszku, miks mleczno-jajowy, przechowywanie