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ScienceDirect
Journal of Food Engineering 87 (2008) 522–526
JOURNAL OF FOOD ENGINEERING
www.elsevier.com/locate/jfoodeng

Preserving functional properties of hen's egg yolk during freeze-drying

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Received 9 November 2007; received in revised form 2 January 2008; accepted 11 January 2008
Available online 18 January 2008

Abstract

A novel freeze-drying process for egg yolk was developed, including precrystallisation and full contact rapid freezing, which is able to reduce the freeze induced gelation to a minimum without ingredients. Conventional pasteurisation conditions (temperatures up to 68 °C) showed to be critical for the preservation of the functional properties of freeze-dried yolk. In combination with optimised pasteurisation conditions (64 °C, 2 min), the results in relative viscosity maximum (the rose of the egg yolk), heat induced gel strength and flow behaviour tally well with those of refrigerated liquid yolk. For the first time, a freeze-dried egg yolk with preserved functional properties and natural taste could be produced at standard costs without ingredients.

Keywords: Egg yolk; Freeze-drying; Gel strength; Viscosity; Pasteurisation; Functional properties

1. Introduction

Egg yolk is an important source of highly nutritional and functional ingredients in a wide variety of food products. The many uses of egg yolk products in the food industry are basically a result of three functional properties: manufacture and stabilisation of emulsions, foaming stability and thermal gelation. The functional properties as well as the quality of the final products are highly influenced by the rheological properties of the yolk-containing phase (Gallegos and Franco, 1999). Therefore, knowledge of the rheological properties of yolk products is important for its commercial applications. The rheological behaviour of egg yolk showed itself to be pseudo plastic and dependent on temperature (Telis-Romero et al., 2006). Within a high temperature range of 55–95 °C diluted egg yolk first showed a viscosity maximum (75–80 °C), followed by a viscosity minimum, before the irreversible aggregation of the proteins began at temperatures above 85 °C. This temperature range is very important for estimating the functional properties of egg yolk (Ternes and Werlein, 1987a).

The volume of liquid egg and egg yolk used in formulations increases constantly. In 2005, approximately 32% of all eggs produced in the USA were further processed for food service, manufacturing, retail and export. Although the production of frozen eggs has levelled out, some growth has been noted in dried egg production (American Egg Board, 2007). Egg yolk is usually dried by spray-drying. However, the dramatic increase in surface combined with temperatures above 54 °C over several days leads to thermal denaturation of proteins. As a consequence of this, spray-dried egg yolk shows enormous impairment in important functional properties. That is why the usage of spray-dried egg yolk in commercial food processing is rather limited.

Another common method of conserving food is by freezing. But, after freezing/thawing egg yolk assumes a gel-like behaviour with rheological characteristics typical of physical gels, where the network is held together by linkages weaker than covalent ones. The gelation process proved to be highly dependent on frozen storage temperature.

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doi:10.1016/j.jfoodeng.2008.01.006

Nomenclature

K	consistency index
LDL	low density lipoprotein
n	flow behaviour index
N	number of measurements
Greek letters	
η	viscosity (Pa s)
η_{rel}	relative viscosity maximum (Pa s)
σ	shear stress (Pa)
$\dot{\gamma}$	shear rate (s^{-1})

Although already starting at −7 °C, the freeze induced gelation mainly occurs in the range of −10 °C to −14 °C (Powrie et al., 1963; Telis and Kieckbusch, 1997). Ice formation and associated freeze concentration of the unfrozen phase disturbs the original structure of yolk, presumably the micellar arrangement of LDL, which is the major component responsible for egg yolk gelation (Powrie et al., 1963; Sato and Aoki, 1975; Wakamatu et al., 1980). Freezing reduces the concentration of water by forming ice crystals, which leads to partial dehydration of proteins, coupled with a rearrangement of lipoproteins. The dehydrated proteins aggregate and form a three-dimensional linked network with micro structural inhomogeneities (Chang et al., 1977; Miyawaki et al., 1992). As a consequence of the freeze induced gelation, frozen/thawed egg yolk forms a gel-like, gummy structure, which can be prevented only by high dosages (up to 10%) of edible ingredients such as salt or sugar. However, the substantial change in taste of these yolk products allows limited substitution only. Another method of preventing the freeze induced gelation is rapid freezing of the yolk by dropping it into liquid nitrogen (Bindrich et al., 1996). It was shown that the loss of functional properties decreases with the yolk droplet size. Nonetheless, the high costs of liquid nitrogen and the gelation during thawing hinders commercial application for these rapid frozen yolk products decisively. As a consequence of this, currently there are no frozen or freeze-dried egg yolk products commercially available. Thus, the aim of this study was to develop a new freeze-drying process of yolk, which allows the functional properties of egg yolk to be preserved without ingredients and liquid nitrogen. The resulting freeze-dried yolk should at least be comparable in functional properties and usage to refrigerated liquid yolk.

2. Materials and methods

2.1. Egg yolk samples

All shell eggs were purchased from a local store and stored in a refrigerator at 8 °C. The yolks of 10 (20, if pasteurised later on) freshly broken shell eggs (less than 10 days of lay) were washed with distilled water to remove the egg white. The water content was determined in an oven by gravimetry (6 h, 105 °C), resulting in 51.3 (±0.35)% (wet basis). Since commercially available refrigerated liquid yolk products contain 10–14% egg white (Mohr and Simon, 1992), 10% egg white was added to the washed yolk samples. The pasteurisation temperature, commonly used in the yolk processing industry, differs from 60 °C to 68 °C and the holding time from 3 min to 10 min (Kulozik and Daimer, 2007). According to this, pasteurisation was carried out at a temperature of 64 °C for 2 min using a self-made tunnel pasteurisation system, equipped with a water thermostatic bath N2 (Haake, Germany) to heat the yolk up to 50 (±0.1) °C, a preheating tube (0.8 cm × 20 cm) to heat the yolk up the 64 °C and a holding tube (0.8 cm × 51 cm) to hold the pasteurisation temperature for 2 min. The glass tubes were heated using a water thermostat Klixon MX 110 (Lauda, Germany) with a stability of ±0.2 °C.

The water content of the pasteurised yolk (blended with egg white 10%) was: 54.1 (±0.1)%.

Conventionally pasteurised refrigerated liquid egg yolk was purchased in 1 L Tetra Paks® (Wiesenhof, Germany). The water content resulted in 59.1 (±0.27)%.

The precrystallised egg yolk was thawed before testing the functional properties.

2.2. Freeze-drying

Initially liquid yolk was prefrozen in round plates (22 cm × 0.2 cm) at −6.3 °C (±0.5 °C) for at least 2 h in a Comfort Plus freezer (Siemens, Germany) with an external temperature control. The following rapid freezing process was carried out with a self-made full contact freezer, consisting of two metal plates, filled with silicon oil and equipped with a RP 870 cooler (Lauda, Germany) at a temperature of −45 °C for 1 min. After that, two frozen yolk plates were freeze-dried at a time with a Lyovac GT2 (Leybold-Heraeus, Germany), equipped with a Triva D4B vacuum pump (Leybold, Germany) and a FP 80 cooler (Julabo, Germany). According to Riedel (1972), 87% of the water content of egg yolk is frozen at a temperature of −20 °C. A decrease in temperature does not lead to a further increase of the ice content. Since the temperature of the egg yolk is already less than −20 °C, after the rapid freezing process, there was no need to choose a temperature below that. Considering the fact of a discontinuous system and the danger of yolk gelation at temperatures above −14 °C, the temperature was set to −25 °C. The drying time of 5 h was a result of measuring the water content during the drying process, ensuring a value below 5%. The remaining water content of yolk after freeze-drying was 2.7 (±0.49)%. The freeze-dried yolk was rehydrated before measuring the rheological behaviour.

2.3. Rheological behaviour

Rheological measurements were carried out using a Physica UDS 200 (Anton Paar, Germany) rheometer, equipped with a parallel & plate measuring system (DIN 53018-1, 50 mm radius, 0.6 mm gap). To control the temperature a TEK 150P/UDS (Anton Paar, Germany) peltier element was used (max. dev. ±0.2 °C).

Flow behaviour of diluted (40%, v/v) native and processed (pasteurised, freeze-dried/rehydrated) yolk samples was studied at shear rates between 1 and 500 s^{-1} at a temperature of 30 °C. Flow curves fitted according to the power law model:

$$\sigma = K \cdot \dot{\gamma}^n \tag{1}$$

The accuracy of the viscometer was checked using Newtonian viscosity standard specimen 2000 AW (ZMK-Analytik-GmbH, Germany) at different temperatures (20 °C, 30 °C and 40 °C).

2.4. Relative first viscosity maximum (the rose of the egg yolk)

Viscosity was measured at a constant shear rate of 26 s^{-1}, in a temperature range of 30–100 °C. At the first viscosity maximum (75–80 °C), diluted yolk (40%, v/v) reaches a point of optimal consistency and foam stability, also known as the "the rose of the egg yolk", because blown on a wooden spoon it appears as a rose flower (Ternes, 1988). According to Ternes and Acker (1994), the first viscosity maximum is a result of the heat induced unfolding of the livetins, which interact with plasma lipoproteins. A gel-like structure is formed, which stabilises yolk foams (Ternes and Werlein, 1987b). Therefore, the intensity of the viscosity increase leading to the first viscosity maximum is an important indicator for the functional properties of egg yolk. The relative viscosity maximum was evaluated as the difference between viscosity minimum and first viscosity maximum.

A low-viscosity paraffin oil (25–80 mPa s) (AppliChem, Germany) was chosen as a sealing fluid for all the measurements in order to avoid coagulation of the protein at the yolk surface. The contribution of the sealing fluid to the viscosity of the samples was found to be negligible.

2.5. Heat induced gel strength

Diluted yolk (1.5 g freeze-dried yolk + 4.5 g water, 3 g liquid yolk + 3 g water) was heated at 80 °C for 20 min in a water thermostatic bath 3041 (Kottermann, Germany), followed by cooling at 20 °C for 10 min in a water bath. Heat induced gel strength was carried out using a penetrometer (OFD, Germany), equipped with upside down conical-frustum shaped stainless steel probe (diameter of upper base: 1.9 cm, diameter of lower base: 1.0 cm). The probe was manually placed on the yolk surface (diameter: 2.7 cm) and allowed to penetrate the yolk gel. The intensity of the penetration was registered on the penetrometer in mm. A deep penetration points out a rather weak heat induced gel. Since thermal gelation is one of the key functional properties of egg yolk, penetration is an important method for evaluating the influence of yolk processing.

2.6. Statistics

All experiments were replicated at least six times. The results are presented as a mean with $N = 6$. Statistics such as linearity test (Mandel), outlier-test (Grubbs), F- and t-tests were carried out using SYSTAT SigmaPlot 10 and Microsoft® Office Excel 2003. Significant differences between means were assessed using ANOVA (p-value < 0.01).

3. Results and discussion

3.1. Precrystallisation

According to Riedel (1972), 81% of the water content of egg yolk are crystallised at a temperature of −6 °C. Assuming a water content of egg yolk of 51% and considering the specific heats from all major yolk components (from 0 °C to −6 °C), approximately 151 kJ are needed to precrystallise 1 kg egg yolk. As a result of a further decrease in temperature (below −14 °C), 5% of the water content of egg yolk are crystallised in addition, requiring approximately 24 kJ/kg yolk for it. Consequently, precrystallisation already removes 86% of the required heat to cool 1 kg egg yolk down to −14 °C. The remaining heat (14%) can easily be removed by rapid freezing, allowing yolk to pass the critical temperature range (−10 °C to −14 °C) in less than 5 s. The precrystallised yolk was thawed before testing the functional properties.

As can be observed in Table 1, precrystallised/thawed yolk showed no significant changes in functional properties and rheological behaviour in comparison to fresh yolk. The relative viscosity maximum and the heat induced gel strength showed only significant differences between native and pasteurised yolk. Therefore, heat treatment during pasteurisation led to a loss in foaming stability and a remarkable degree of denaturation of yolk proteins, resulting in weaker heat induced protein networks and higher penetration values.

3.2. Rapid freezing and freeze-drying

With the full contact freezer, the precrystallised yolk plates pass the critical temperature range in less than 5 s (see Fig. 1). If not freeze-dried immediately afterwards,

Table 1
Influence of precrystallisation on functional properties and flow behaviour of native and pasteurised egg yolk

	Egg yolk			
	Native	Precrystallised	Pasteurised	Pasteurised and precrystallised
Relative viscosity maximum (Pa s)	2.5 ± 0.12	2.5 ± 0.12	2.0 ± 0.13	2.0 ± 0.09
Penetration value (mm)	1.9 ± 0.37	1.7 ± 0.20	2.9 ± 0.14	2.5 ± 0.29
Consistency index (Pa s^n)	0.014 ± 0.005	0.014 ± 0.004	0.033 ± 0.004	0.033 ± 0.006
Behaviour index	0.99 ± 0.05	1.00 ± 0.02	0.91 ± 0.03	0.92 ± 0.06

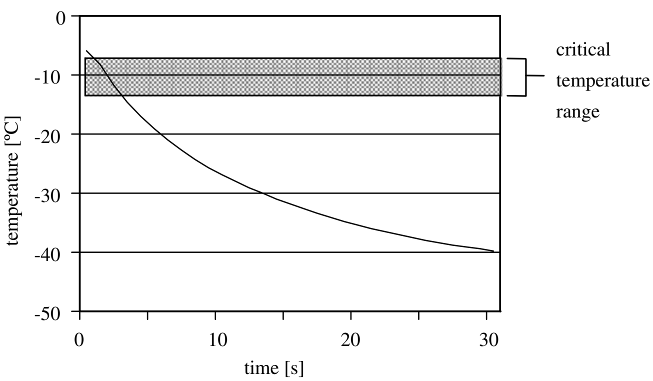

Fig. 1. Decrease in temperature during rapid freezing of egg yolk (starting at −6 °C, after the precrystallisation process).

the frozen yolk can be stored at −20 °C up to 13 h without structural changes, which allows discontinuous processing.

Fig. 2 shows the results of the relative viscosity maximum. After freezing/thawing the value decreased dramatically, especially for the pasteurised yolk. However, the loss in relative viscosity maximum after freeze-drying/rehydrating is considerably smaller and does not significantly differ from freshly pasteurised yolk. Since there is a positive correlation between the gel-like structure from the first viscosity maximum and the foam stability of egg yolk (Ternes and Acker, 1994), it can be assumed that freeze-drying definitely contributes to preserve the foam stability of egg yolk. These results tally well with those from the heat induced gel strength. Unlike freeze-dried yolk, frozen/thawed yolk showed a significant decrease in gel strength (Fig. 3). This indicates a considerable loss in the ability to produce a stable three-dimensional network of yolk lipoproteins. Nonetheless, denaturation of yolk proteins can be

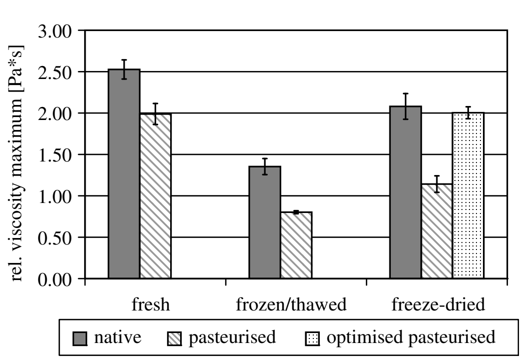

Fig. 2. Change in relative viscosity maximum of egg yolk depending on the conservation process. Error bars represent the standard deviation.

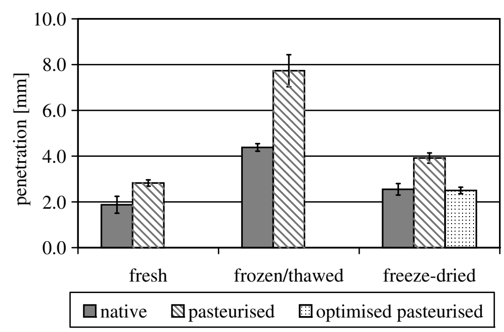

Fig. 3. Change in heat induced gel strength of egg yolk depending on the conservation process. Error bars represent the standard deviation.

decisively reduced by freeze-drying. The penetration value for freeze-dried/rehydrated yolk showed no significant increase in comparison to fresh yolk.

Pasteurisation plays a key role in the quality of frozen or freeze-dried yolk. Predamage to yolk proteins, caused by high temperature pasteurisation (temperatures up to 68 °C is quite common for refrigerated liquid yolk) strongly intensified the loss in functional properties of frozen or freeze-dried yolk. By optimising the pasteurisation conditions (64 °C, 2 min) the heat damage can be considerably reduced as the values for the relative viscosity maximum and the heat induced gel strength show. Pasteurisation at temperatures higher than 64 °C, followed by freeze-drying, resulted in the complete inability to produce a sabayon, a wine flavoured yolk foam, which is characterised by its thick and foamy consistency (Bickel, 1984).

Although the flow behaviour of yolk changed remarkably after freeze-drying/rehydrating, the difference is smaller compared to frozen/thawed yolk. Table 2 shows the change in consistency and behaviour indexes. As a result of the freeze induced gelation, the consistency index increased, whereas the flow behaviour index decreased significantly. With a flow behaviour index below 1, freezing/thawing changed the rheological behaviour of diluted yolk from Newtonian to shear-thinning (pseudo plastic) behaviour. Pasteurisation does not affect the flow behaviour significantly.

Besides, the heat induced gel strength proved to be highly dependent on the water content remaining in the dried yolk powder. As presented in Fig. 4, there is a linear correlation between the penetration value and the water content. Aside from increasing the microbiological stability, the water content should be less than 6%. At values below 5.8% the water is completely bound and the yolk

Table 2
Influence of the freeze-drying and freezing/thawing process on the flow behaviour of native and pasteurised egg yolk

	Egg yolk				
	Freeze-dried[a]	Frozen/thawed[a]	Freeze-dried[b]	Frozen/thawed[b]	Freeze-dried[c]
Consistency index (Pa s^n)	0.16 ± 0.03	0.28 ± 0.04	0.14 ± 0.01	0.32 ± 0.11	0.14 ± 0.02
Behaviour index	0.78 ± 0.02	0.67 ± 0.02	0.79 ± 0.01	0.63 ± 0.03	0.78 ± 0.03

[a] Native yolk.
[b] Pasteurised yolk (refrigerated liquid yolk).
[c] Optimised pasteurised yolk.

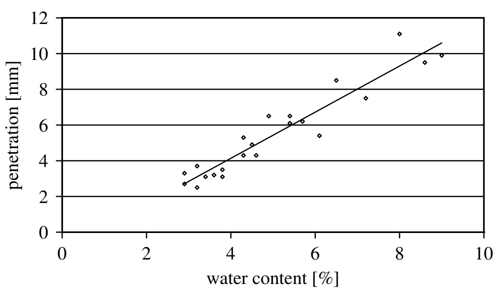

Fig. 4. Correlation between the water content remaining in the dried yolk and the heat induced gel strength.

proteins are stabilised in the so-called glass condition during thawing (Powrie et al., 1963). At higher water content values, changes in yolk proteins lead to a loss in the ability to produce a stable three-dimensional network. As a consequence of this, the penetration value increases.

4. Conclusion

Egg yolk which had passed through a precrystallisation/thawing process is not significantly affected in rheological behaviour and heat induced gel strength.

Unlike freeze-dried egg yolk, frozen/thawed egg yolk showed an enormous loss in relative viscosity maximum and heat induced gel strength. Using conventionally pasteurised egg yolk, such losses were highly intensified, even during freeze-drying.

In combination with optimised pasteurisation conditions (64 °C, 2 min), the results in relative viscosity maximum, heat induced gel strength and flow behaviour showed no significant differences between freeze-dried and refrigerated liquid yolk. Therefore, freeze-drying, including precrystallisation and full contact rapid freezing allows the functional properties of egg yolk, without ingredients, to be preserved. Since full contact rapid freezing makes it possible to do without liquid nitrogen, freeze-dried egg yolk can be produced even at marketable costs.

Acknowledgements

This work was supported by the German Ministry of Economics and Technology (via AiF) and the FEI (Forschungskreis der Ernährungsindustrie e.V., Bonn). Project AiF 14259 N.

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