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Egg yolk gels: Sol-gel transition and mechanical properties as affected by oleuropein enrichment

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ABSTRACT

The effect of oleuropein on the gelation properties of whole egg yolk at different pHs (2, 4.5 and 6.4) was studied. Egg yolk solutions were added with increasing amount of pure oleuropein, gelled by either thermal (pHs 4.5 and 6) or acid gelation (pH 2) and submitted to frequency sweep and stress relaxation tests. The experimental data obtained by the frequency sweep tests were modeled with a power law equation in order to get the co-ordination number z and the proportional coefficient A, which describe the network extension and its strength, while data obtained from stress-relaxation tests were fitted by a generalized Maxwell model with 5 elements. The addition of oleuropein affected the gelation behavior as well as the rheological properties of the gel network, and the effect was influenced by the pH of the systems. A shift of the gel point towards lower temperatures was observed in the presence of the phenolic compound, and this effect was significant in the systems at pH 4.5 (from 72.55 ± 0.07 °C to 70.43 ± 0.06 °C). According to the results obtained from the modelling of the frequency sweep test, gels at pH 6.4 and 2 were characterized by a weak network; on the contrary, at pH 4.5 the network was characterized by a low number of flow units (lower z, z = 16.52 on average) interacting with one another in a more strictly way (higher A, A = 5362 Pa $s^{1/z}$ on average). Such findings were successively confirmed by the stress relaxation results where it was shown that firmer gels were obtained at pH 4.5 after oleuropein enrichment.

1. Introduction

Hen egg yolk (EY) is an important ingredient of a wide variety of food products thanks to its high technological functionality. Besides the excellent emulsifying activity, EY ability to undergo a sol-gel transition under thermal treatments or acidic conditions is the basis of major applications such as bakery products, egg-based sauces and creams (Kiosseoglou & Paraskevopoulou, 2005).

EY is a complex association of lipids and proteins in water in which several types of particles are suspended in a protein solution or plasma. It is characterized by different structuration levels consisting in non-soluble protein aggregates (granules) in suspension in a clear yellow fluid (plasma) that contains low-density lipoproteins (LDLs) and soluble proteins. Granules represent about 22% of yolk dry matter, accounting for about 50% of yolk proteins and 7% of yolk lipids and are mainly constituted by high-density lipoproteins (HDLs) (70%) and phosvitins (16%) linked by phosphocalcic bridges (Anton, 2013). Plasma corresponds to about 78% of yolk dry matter and is composed of 85% LDLs and 15% livetins. It accounts for about 90% of yolk lipids (including nearly all the carotenoids) and 50% of yolk proteins (Laca, Paredes, & Díaz, 2011).

Protein gelation is one of the most important mean to obtain desiderable sensory, textural and structural properties in foods; as far as yolk gelation is concerned, its mechanism is mainly dominated by plasma constituents such as livetin and LDL proteins (Kiosseoglou & Paraskevopoulou, 2005). Changes in the physical properties of egg yolk-based heat-set gels can be due to different technological factors such as pH, ionic strength and the presence of solutes (Cordobés, Partal, & Guerrero, 2004; Raikos, Campbell, & Euston, 2007) or any other ingredient that can interact with protein molecules and affect their behavior.

In the past decades polyphenols have become an intense focus of research interest due to their health-beneficial and preventive effects towards several chronic diseases (Williamson, 2017) and increasing is the demand of functional products enriched with phenolic extracts or formulated with raw materials naturally rich in such bioactives. Besides

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their bioactivity, attention is being paid also to the technological functionality of phenolic compounds in complex and colloidal systems. Among others, those derived from olives and olive oil were in fact shown to influence the emulsification process in both model emulsions (Di Mattia, Sacchetti, & Pittia, 2011; Di Mattia et al., 2014) and real complex formulations such as mayonnaise (Di Mattia et al., 2015; Giacintucci, Di Mattia, Sacchetti, Neri, & Pittia, 2016). The effect was ascribed to the surface properties of phenolic compounds, oleuropein in particular, and to the occurrence of protein-polyphenol interactions; polyphenols are in fact known to form complexes with proteins leading to changes in the structural, functional and nutritional properties of both compounds (Jacobek, 2015). Several models have been proposed to explain protein-polyphenol interactions suggesting that such complexes are mainly formed by weak interactions, mostly of hydrophobic nature, between aminoacids side chains and polyphenol aromatic ring and can be further stabilized by the presence of hydrogen bonding (von Staszewski, Jagus, & Pilosof, 2011). The parameters that are defined to affect protein–phenolic interactions are basically temperature, pH, protein type and concentration, and the type and structure of phenolic compounds.

However very few works are present in the literature about the effect of protein-polyphenol interactions on protein functional properties, especially the ones related to egg yolk gelation. Indeed, to date, protein-polyphenol interactions has been studied mainly on milk, meat and some plant proteins and scarce are the studies where egg yolk was investigated. The aim of this work was thus to provide useful information on the sol-gel transition, as well as on the mechanical characteristics of EY gels as affected by the enrichment with oleuropein, one of the major olive phenolic compound. For this purpose, oleuropein was added to EY, and its contribution to heat-induced or acid-induced network formation was observed at different pH, namely pH 2, 4.5 and 6.4. The pH 6.4 is approximately the natural pH of egg yolk whilst pH 4.5 corresponds to a typical pH that can be obtained in most salad dressing emulsions. The pH 2 was then chosen to explore the effect of oleuropein addition on the acid-induced egg yolk gel. To better understand the mechanical spectra of the systems under investigation, two different rheological tests were performed on selected systems: frequency sweep and stress-relaxation tests.

2. Materials and methods

2.1. Materials

Hen's eggs (quality category A) were purchased from a local supermarket; eggs from the same producer and type of husbandry were used throughout the experiments. Analyses were usually carried out within 2 weeks from the date of deposition; during this time, samples were stored at 4 °C until use. Oleuropein was from Extrasynthese (Lyon, France). Ultrapure water from the USFELGA water purifier system from Purelab Plus (Ransbach-Baumbach, Germany) was used throughout the experiments. Sodium acetate and glacial acetic acid were purchased from Sigma-Aldrich (Steinheim, Germany). All the reagents were of analytical grade.

3. Methods

3.1. Sample preparation

Eggs were manually broken and the yolk carefully separated, taking care of removing the egg white and chalazae. Three egg yolks from the same batch were pooled and gently stirred using a spatula. Seven batches of eggs from each type of husbandry (classes 0–3; size L, quality A, each) were obtained from local supermarkets. Before the analysis, a 1:2 (w/w) dilutions of the EY was performed by using different solvents according to the pH required on the final sample. Ultrapure water and 0.5 M acetate buffer were used to obtain the pH 6.4 and 4.5 samples, respectively. For the pH 2 systems, glacial acetic acid was used for pH correction. The following oleuropein concentrations were tested: 250, 500 and 1000 ppm. To allow a complete solubilization, oleuropein was previously added in the solvent phase. Dilutions were done in order to ensure the same yolk content in all the samples.

3.2. Thermal gelation

The thermal gelation was carried out by using a rotational rheometer MCR 320 (Anton Paar, Austria), equipped with a plate/plate measuring system (PP50). Samples were poured onto the bottom plate of the measuring system, with a gap of 0.9 mm. The temperature of the bottom plate was controlled with a Peltier system (C-PTD200), and paraffin oil was applied to the exposed surfaces of the sample to prevent evaporation. During gelation, storage and loss moduli were measured; the frequency was 1 Hz and the strain was set to 0.1%, a value within the linear viscoelastic region determined in preliminary experimentation.

Before performing the thermal ramp, the temperature of the samples was equilibrated, until reaching a constant value of 30 °C for 1 min; temperature ramps were carried out from 30 °C to 90 °C with a heating rate of 5 °C/min. After reaching 90 °C, the temperature was maintained for 5 min. Samples were cooled (10 °C/min) to 30 °C and kept at this final temperature for 10 min. The EY gels obtained with such procedure were then used for dynamic oscillatory measurements and relaxation tests. No thermal gelation was carried out on pH 2 systems.

3.3. Frequency sweep

Frequency sweep tests have been carried out on coagulated protein gels at a constant temperature of 30 °C. Frequency sweeps were carried out from 0.1 to 40 Hz, and a constant shear strain of 1% was applied, according to the work of Laca, Paredes, and Díaz (2011). The rheological parameters used for this study were the storage (G′), the loss (G″) and the complex (G*) moduli. The experimental data of all frequency sweep tests were fitted by the following power law equation (Gabriele, De Cindio, & D'Antona, 2001):

$$G*(\omega) = \sqrt{G'(\omega)^2 + G''(\omega)^2} = A\omega^{1/z} \quad (1)$$

where G* is the complex modulus in Pa, ω the frequency in Hz, z the coordination number (dimensionless) and A the coefficient of proportionality (Pa $s^{1/z}$).

3.4. Stress-relaxation tests

The viscoelastic behavior of the EY samples coagulated either by using the procedure previously described or by acidic conditions, were analyzed by stress-relaxation tests at a constant temperature of 30 °C. In the first step, the sample was kept under a constant shear strain of 1% for 10 min; in the second one, the shear strain was reduced to 0% for 5 min; in the third one, the shear strain was increased to 20% and kept for 10 min; then, in the fourth and last step, the shear strain was decreased again to 0% and kept on hold for 5 min. In all steps, shear stress was determined as a function of time. Results were fitted by the generalized Maxwell model with five elements and a residual spring element in series as follows:

$$\sigma(t) = \sigma_e + \sum_{i=1}^{5} \sigma_i \exp\left(\frac{-t}{\lambda_i}\right) \quad (2)$$

where σ(t) is the stress over the time of analysis (t), i is the number of Maxwell bodies, σ_i is the elastic modulus of the springs in Maxwell body, λ_i is the relaxation time of the Maxwell body and σ_e is the elastic modulus of the lone spring.