

RHEOLOGICAL PROPERTIES OF AGEING EGG YOLK

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Abstract

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The rheological behaviour of egg yolk after different storage periods and temperatures was investigated using rotational viscometer. The eggs were stored for 1, 2, 3, 4 and 8 weeks at constant temperatures: 4 °C, 8 °C, 12 °C and 16 °C. The apparent viscosity was measured as a function of shear rate. For given shearing rate, the viscosity was measured in dependence on shearing time. The decrease of viscosity with storage time is attributed to the balance of different osmotic pressure from yolk and albumen of fresh egg. The yolk (with higher dry matter than albumen) absorbs water from albumen through vitelline membrane. It was found that yolk samples exhibited shear-thinning and thixotropic behaviour. The shear-thinning behaviour was fitted well into simple models. The resting of sample at room temperature caused increase of viscosity. This effect is explained by drying off of testing yolk, the regeneration of yolk structures and changing chemical composition during resting. The time-dependant viscosity decreased rapidly with time and at lower shear rates reached an equilibrium stage. The time-dependant viscosity was also found to decrease with storage time. The value of pH was changed (increased) during storing. No clear dependence between pH value and viscosity was confirmed.

egg yolk, rheological behaviour, viscosity, shear rate, time-dependant flow, pH, modelling

The word “rheology” was first used by Eugene C. Bingham (circa 1928) who also described the motto of the subject as $\pi\alpha\nu\tau\alpha \rho\epsilon\iota$ (“panta rhei”, from works of Heraclitus about 500 B.C.) meaning “everything flows” (Reiner, 1964). Rheology is now well established as the science of the deformation and flow of matter.

Indispensable part of this science is food and food materials rheology which could be also described as a material science of food. There are numerous areas where rheological data are needed in the food industry or in agriculture.

And one of common agricultural products widely used in food (but not only) industry is egg yolk. The use of egg yolk in different applications is extremely wide and knowledge of its physical and mechanical properties (including rheological) seems to be critical. Egg yolk is for example used as a functional and nutritional ingredient in food products. Main compo-

nents of egg yolk are triacylglycerols, phospholipids, proteins, and carbohydrates.

LITERATURE REVIEW

Many unique rheological properties of various foods and related materials have been summarized in books (Rao and Steffe, 1992 and Weipert et al., 1993). General overview of rheological (and other) are summarized in (Welti et al., 2002). Reliable and accurate rheological characterization of foodstuffs, particularly time-dependant effects, is required for the control of quality, texture, and shelf-life, and for the design of processing equipment. This problematic is described in (Dimonte et al., 1998). Fluids such as air and water have a simple flow behaviour which is independent of the previous process history of the material. Foodstuffs are more complex, and their flow behaviour may depend on the way they have been previously processed (Rielly, 1997). Modelling of time-de-

pendant rheological behaviour of biological materials and food is quite necessary for complete knowledge of material characterization. This problematic is discussed e.g. in (Abu-Jdayil, 2002 and 2003; Donnel, 2002; Juszczak et al., 2004 and others). Important influence changing rheological properties of foods is their previous processing (Valencia et al., 2002).

Several studies have investigated the physical and chemical properties of yolk, but most studies have concentrated on microbiological analysis (Denys, 2004; Sancho, 1999 or Martucci, 1997).

MATERIAL AND METHODS

Observing of rheological properties was only a part of a complex research focused on evaluating of properties and quality of maturing eggs.

The eggs of two brown egg-laying breeds have been monitored. In particular: Bar Plymouth Rock, denoted as BPR and Rhode Island Red, denoted as RIR. Laying hens have been kept in identical conditions of housing namely in laying halls with cage technology. The hens were kept in selection breeding farm.

The eggs have been sampled in 19th and 30th week of laying period in sum of 180 pieces from each breed. The eggs were subsequently stored under different temperatures (4 °C, 8 °C, 12 °C and 16 °C) in unchangeable conditions for the period of 0, 1, 2, 3, 4 and 8 weeks.

Selected samples of yolk were left in room temperature conditions in uncovered container for 1, 2, 3 and 4 days. Viscosity changes were monitored. No samples were analysed after 4 days because of biological degradation of tested material.

The procedure of sample preparation for viscosity measurements was following.

Yolk: The yolk was immediately after separation from albumen bladder cleared with the aid of tweezers from and additionally cleared from all other albumen residues by use of filter paper. This process was followed by removing of yolk membrane and mixing material for two minutes at 2000 rpm. The pH (by use of pH meter) was measured consequently.

Egg white: The composite sample of egg white was after removing of yolk and chalazas mixed by use of small-sized mixer stirred for five minutes at 2000 rpm. The pH was measured by pH-meter.

Although the samples are supposed to be prepared by exactly same procedure in order to achieve identical experiment conditions and comparable results, such goal is extremely difficult to reach. It is necessary to note that authors can not guarantee 100% repeatability and getting completely same measured experiment values. The reason of this impossibility consists in highly changeable biological composition of tested material. Although the samples preparation was

conducted with the highest possible care, there is still individual alternative and chance of slightly different perfection when removing the yolk from albumen sack or removing different residues. Even the smallest differences during sample preparation can consequently cause the relevant variances in viscosity data. Also following part of preparation (mixing the samples for two minutes at 2000 rpm) could create certain changes in viscosity values. Authors accept the matter of fact that rheological data of egg yolk are influenced by such preparation procedure, but on the other hand present the results in connection with introduced method as a way of evaluating the rheological properties of given (mixed yolk) material. As mentioned before, determination of viscosity was just a part of a complex investigation and evaluation of several other characteristics and selected sample preparation is standard method in such cases. The objective determination of yolk viscosity is due to described challenging problems with sample preparation rather questionable. In case of egg white is such determination almost impossible without very clear definition of measured sample (again hardly repeatable) including description of changing presence of different natural constitutives, different phases and other biological influences. The data related to egg yolk or albumen viscosity are very rare in the literature. Some results can be found in (Rao, 1986).

Measuring device

There are several methods to measure dynamic viscosity of fluid or semi fluid materials and different geometries may be utilized: concentric cylinders, cone and plate, and parallel plates.

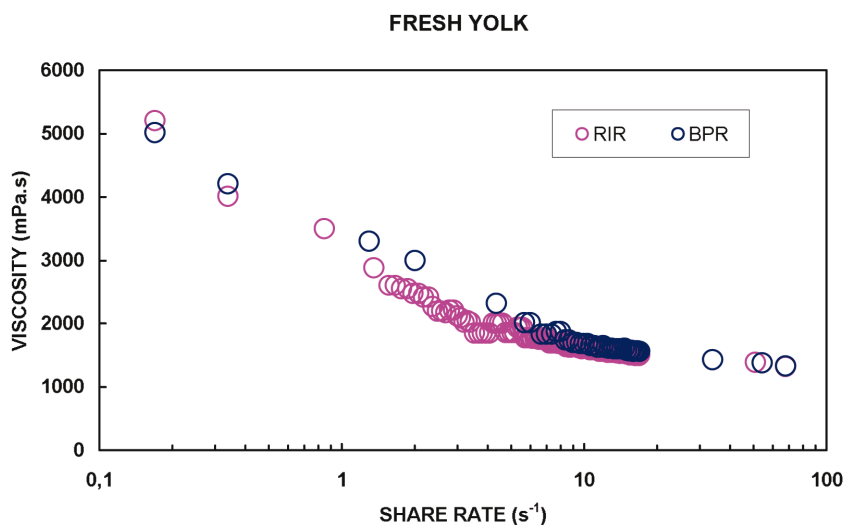
Our laboratory uses Anton Paar DV-3 P Digital Viscometer which is designed to measure dynamic viscosity, shear stress (τ), and shear rate ($\dot{\gamma}$). The DV-3 P is a rotational viscometer, based on measuring the torque of a spindle rotating in the sample at a given speed.

Shear stress is expressed in [g/(cm.s²)], shear rate in [s⁻¹] and viscosity in [mPa.s] speed of spindle in revolutions per minute [rpm].

RESULTS AND DISCUSSION

Viscosity measurement as a function of share rate:

Samples were measured at room temperature (~20 °C). The apparent viscosity of egg yolks of two breeds (BPR and RIR) were measured as a function of strain rate. The measurements were carried out with increasing shear rate. The shear rate varied from 0.17 to 68 s⁻¹. The duration of experiment was generally set to 10 min but other durations were carried out with similar results.



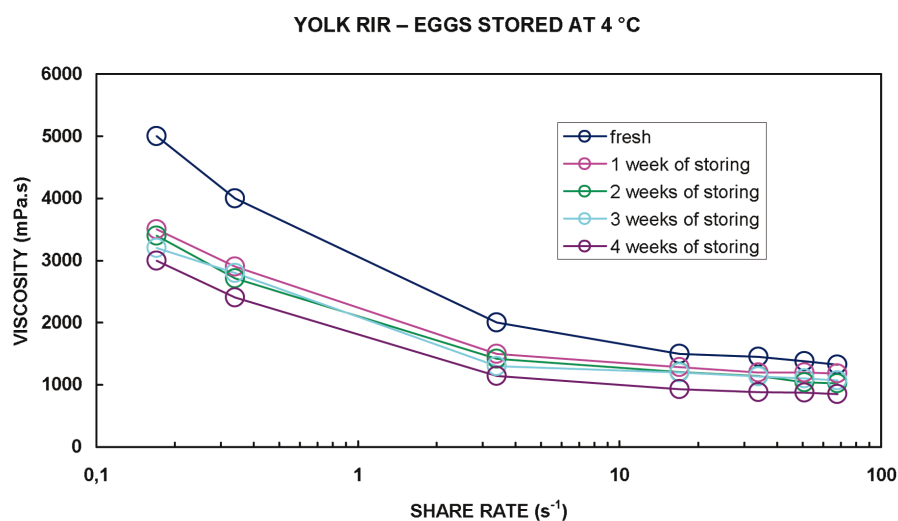
1: Apparent viscosity – share rate dependence for BPR and RIR yolk

Fig. 1 shows the dependence of viscosity on share rate for BPR and RIR yolk. It is obvious that viscosity values are very similar and there is no possibility to identify laying hen breed by determining yolk viscosity. The dependence shows that yolks exhibit shear-thinning behaviour, i.e., the apparent viscosity decreases with shear rate. The shear-thinning behaviour was expected in yolk since its texture is affected by weak physical bonds and hydrophobic interactions (Velez-Ruiz, 2002). Therefore, the fall in viscosity of yolk with shear rate seems to be as a result of destruction of the interactions.

The measurement of increasing shear rate shows a hysteresis loop, which indicates that yolk exhibited a thixotropic behaviour. The thixotropic behaviour is a characteristic of yolk regardless of the storage time. It should be stated here that the hysteresis behaviour cannot be used quantitatively to determine

the effect of storage time on the thixotropic behaviour of yolk.

The effect of storage time on the flow behaviour of yolk is illustrated in Fig. 2. The eggs were kept in a different conditions but presented diagram applies to 4 °C storing temperature. At constant shear rate the viscosity decreases with increasing storage time. The decrease in viscosity of yolk with storage time indicates decreasing number of interactions in yolk structure occurring during storage. Sakanaka et al. (2003) have observed that the complex modulus of yolk (under similar conditions as in the present study) decreased with time. They found the decrease of gel presence with storing time. Their explanation was that, throughout the storage period, component rearrangement was in progress and less contacts were present. It seems that rearrangement of the structure network is responsible for the decrease in the apparent viscosity.



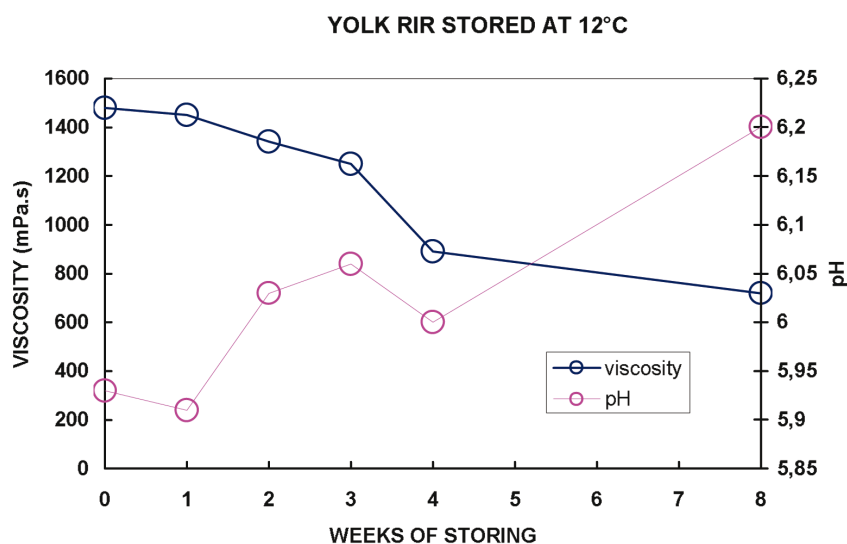
2: Effect of storage time on the viscosity of yolk as a function of share rate

Table I lists the values of pH measured during different stages of maturing (fresh, 1, 2, 3, 4 and 8 weeks) and different storing temperatures (4 °C, 8 °C, 12 °C

and 16 °C) for all kinds of yolk monitored within the experiment.

I: The values of egg yolk pH

Yolk type and storing temperature	Fresh [pH]	1 week of storing [pH]	2 weeks of storing [pH]	3 weeks of storing [pH]	4 weeks of storing [pH]	8 weeks of storing [pH]
BPR stored at 4 °C	6.06	5.93	5.94	6.06	6.08	6.21
RIR stored at 4 °C	5.93	6.01	5.95	6.04	6.04	6.20
BPR stored at 8 °C	5.90	5.98	6.00	6.05	6.07	6.21
RIR stored at 8 °C	5.87	5.96	6.02	5.99	6.04	6.16
BPR stored at 12 °C	6.06	5.97	6.03	6.10	6.03	6.24
RIR stored at 12 °C	5.93	5.91	6.03	6.06	6.00	6.20
BPR stored at 16 °C	5.90	6.05	6.04	6.13	6.04	6.37
RIR stored at 16 °C	5.87	6.07	5.97	6.04	6.14	6.26



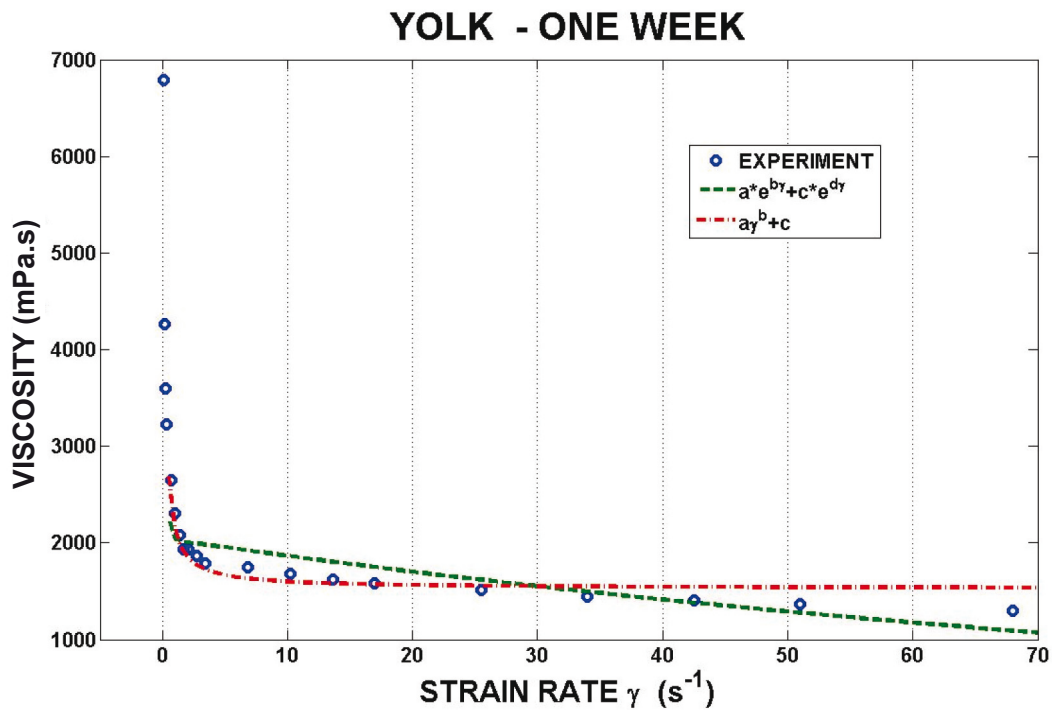
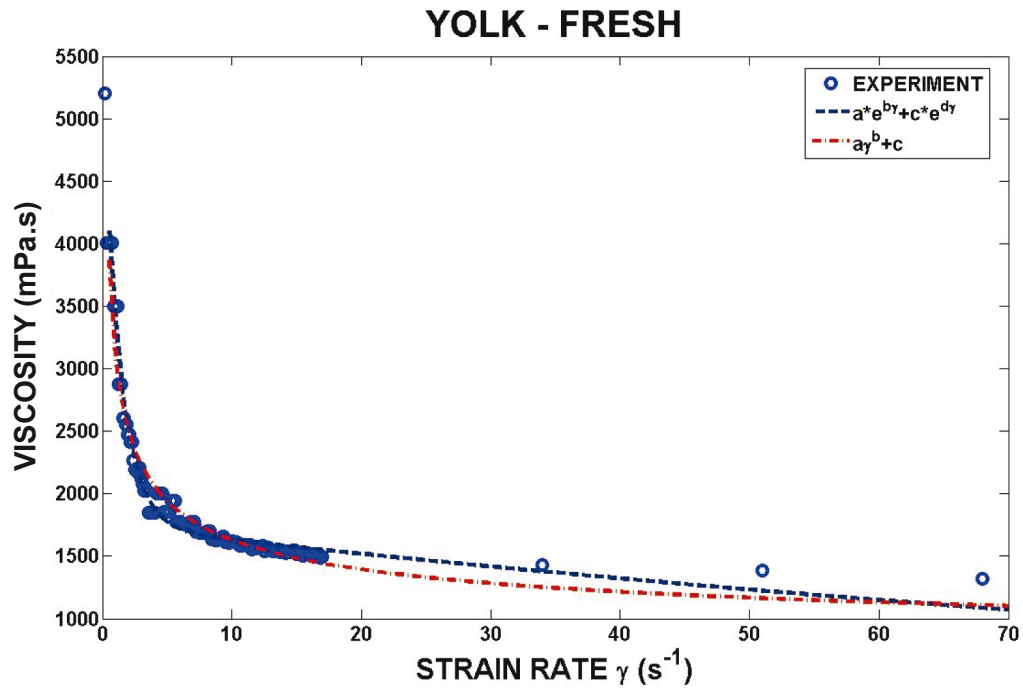
3: Viscosity and pH values varying with storing time

As it is visible on Fig. 3, the value of pH is changing with storing time. Shown diagram displays the values valid for RIR yolk stored at 12°C. Similar diagram could be composed for all the possible combina-

tions of yolk type and storing temperatures. The main characteristics and attributes of the diagram would be similar (rather irregular development of pH). The value of pH is not stable and varies during maturing.

Because of relevant differences between single dependencies, there is not possible to clearly describe the the general relation between pH value and storing time, viscosity alternatively. It could be stated that yolk viscosity value is partly reflecting the pH value,

but an exact definition is not possible. The decrease of viscosity with current increase pH is notable but generally statistically not definable. The decrease of viscosity value wit storing time will be discussed later.



The non-Newtonian viscosity of fresh yolk was modelled using three simple models

$$\eta = a\dot{\gamma}^b + c, \quad (1)$$

where: $a = 2436$ $b = -0.3987$ $c = 654.9$ $R^2 = 0.9582$.

$$\eta = a + \frac{b}{\dot{\gamma}}, \quad (2)$$

where: $a = 1651$ $b = 906.7$ $R^2 = 0.7572$.

$$\eta = a \exp(b\dot{\gamma}) + c \exp(d\dot{\gamma}), \quad (3)$$

where: $a = 3453$ $b = -0.7372$ $c = 1747$ $d = -0.006981$ $R^2 = 0.9774$

To model the flow behaviour and to fit measured data with computed curves, curve fitting application (MATLAB) was used. Measured dependencies and fitted curves are shown on Fig. 4 and 5.

The results of fitting were satisfying in case of model (1) where $R^2 = 0.9582$ and exponential fitting (3) where $R^2 = 0.9774$. These two models are also displayed as blue and red line in Fig. 3. Model (2) did not show a good applicability since $R^2 = 0.7572$ is not as tolerable outcome as the ones showed by models (1) and (3).

Similar procedure was applied to yolk extracted from eggs stored one week at 4°C.

$$\eta = a\dot{\gamma}^b + c, \quad (4)$$

where: $a = 618.2$ $b = -0.9167$ $c = 1525$ $R^2 = 0.9837$.

$$\eta = a + \frac{b}{\dot{\gamma}}, \quad (5)$$

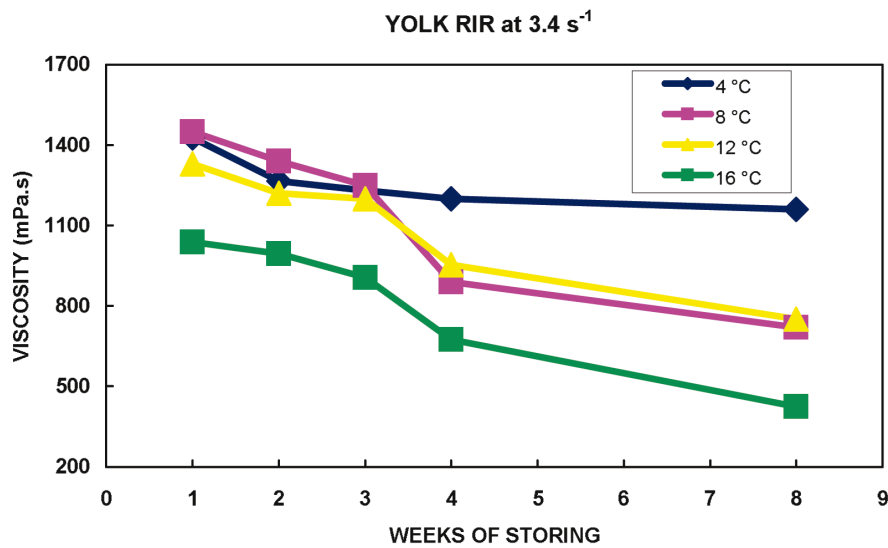
where: $a = 1574$ $b = 517.4$ $R^2 = 0.9825$.

$$\eta = a \exp(b\dot{\gamma}) + c \exp(d\dot{\gamma}), \quad (6)$$

where: $a = 9857$ $b = -7.628$ $c = 2047$ $d = -0.009247$ $R^2 = 0.9598$.

Correlations of all three models confirmed very good suitability of selected constants and chosen forms of models. The highest level of matching ($R^2 = 0.9837$) was reached through model (4). The dependences show the tendency of egg yolks for shear-thinning behaviour when the viscosity decreases with shear rate. Such response is than well predictable with proposed models.

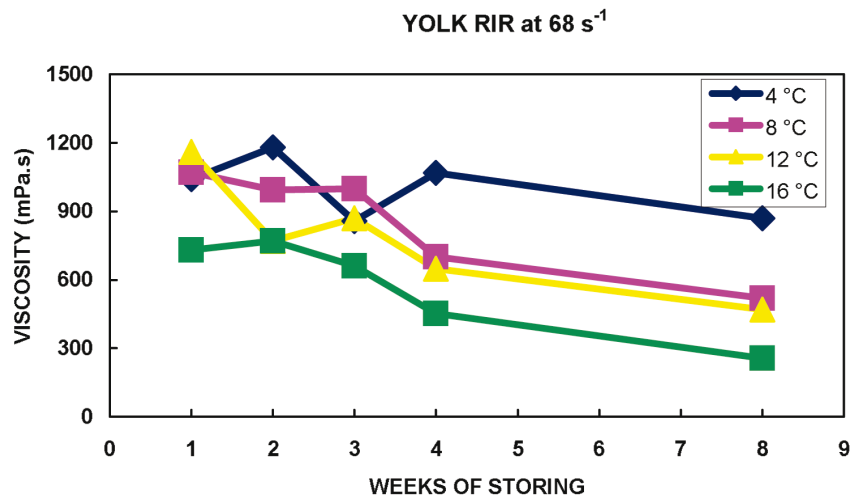
Another effect of storing was evaluated when monitoring the influence of different storing temperature on viscosity of yolk. The eggs were kept in constant temperature conditions for 1, 2, 3, 4 and 8 weeks. The yolks were then examined under two share rates, namely 3.4 s^{-1} and 68 s^{-1} . The first dependence is shown in Fig. 6. To compare received data with the value of fresh yolk could be also a helpful tool. In the case of yolk sheared at 3.4 s^{-1} , this quantity had a value of 2023 mPa.s. As it is evident from the diagram, the clear definition of dependence of yolk viscosity on storing time is not statistically provable. Especially when comparing the values determined after initial periods of storing at 4 °C and 8 °C or final periods of storing at 8 °C and 12 °C. But generally, without specifying particular values, following statement is possible. Egg storing time and temperature influence viscosity of yolk. The viscosity of yolk is decreasing with storing time. Definite decrease of viscosity between the samples stored 1 week (fresh alternatively) and 8 weeks is clearly detectable. Similar statement is possible when evaluating influence of storing temperature. All the samples exhibited viscosity decrease with increasing storing temperature. When combining both impacts (extending storing period and raising storing temperature) the decrease of viscosity is rather important. Exemplifying is possible through comparing viscosity of fresh yolk (2023 mPa.s) and viscosity of yolk separated from egg stored for 8 weeks in 16 °C (425 mPa.s). The viscosity of second mentioned sample shows only 21% of value of fresh sample.



6: Viscosity changing during different periods of storing and different storing temperature. Measured at 3.4 s^{-1} . Viscosity of fresh yolk = 2023 mPa.s .

Next experiment was focused on evaluating of similar dependence at higher value of shear rate, na-

mely 68 s^{-1} . The results of this experiment are plotted in Fig. 7.



7: Viscosity changing during different periods of storing and different storing temperature. Measured at 68 s^{-1} . Viscosity of fresh yolk = 1322 mPa.s .

As well as in the last example, also here is the clear definition of relation between individual effects and influences very complicated. The values measured during first four weeks and after storing at different temperatures are largely irregularly varying. The only temperature where the results are apparently showing decrease of viscosity is the highest

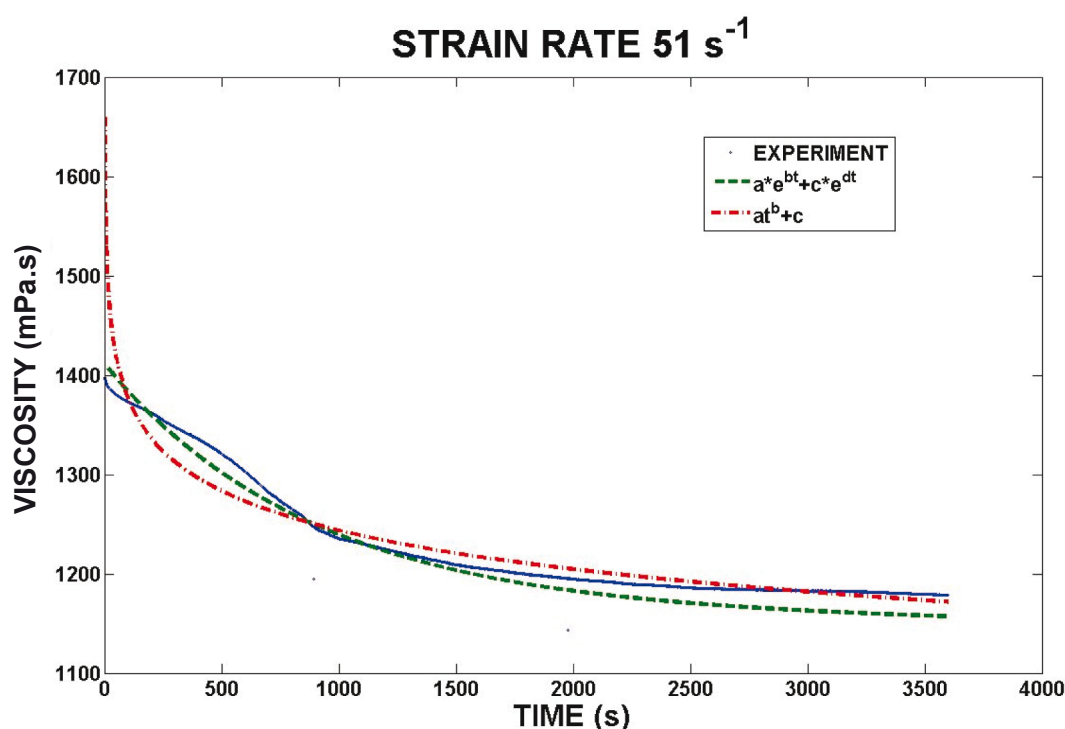
storing temperature ($16 \text{ }^{\circ}\text{C}$) and also the longest storing time (8 weeks) evidently influences the viscosity value. The difference between viscosity of fresh yolk (1322 mPa.s) measured at 68 s^{-1} and viscosity after 8 weeks of storing at $16 \text{ }^{\circ}\text{C}$ (256 mPa.s) is also obvious. The value of second result reaches approx. 20% of first value.

Time-dependent flow properties

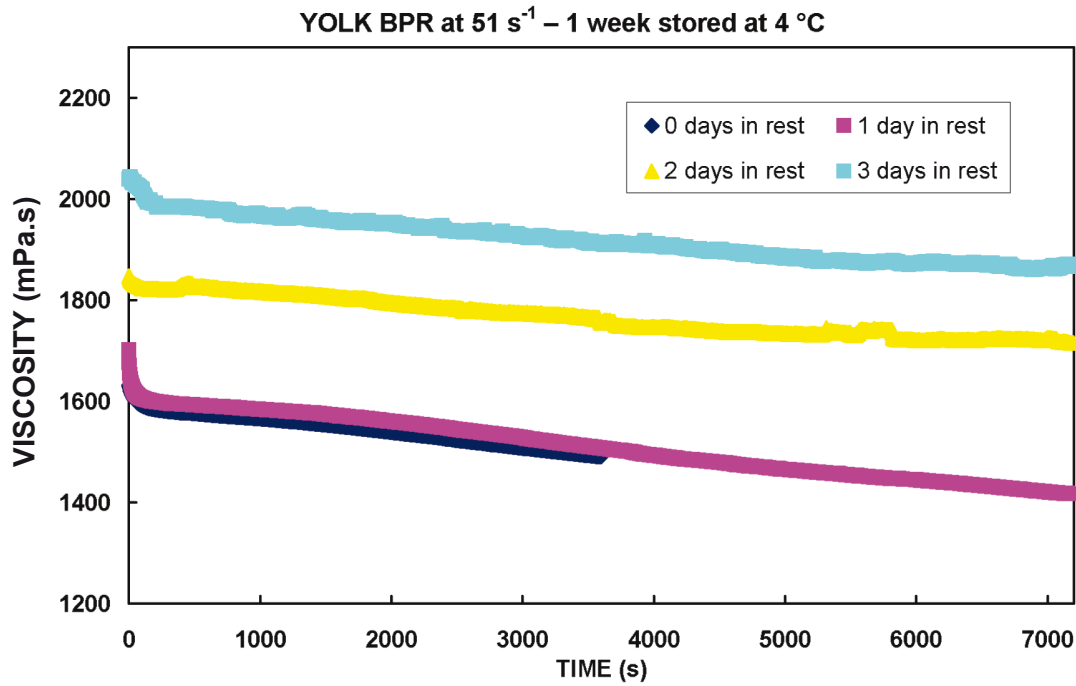
The time-dependent viscosity of yolk was measured at constant shear rates of 0.34 and 51 s⁻¹. Typical experimental results are shown in Fig. 8. and 9. Fig. 9. also compares flow properties of yolks left to rest at room temperature in uncovered container for 1, 2 and 3 days. At a constant shear rate, the apparent viscosity decreases rapidly with time within the first 5 min of shearing and approaches a constant value corresponding to an equilibrium state after approximately 40 min. These results were deduced from comparing several diagrams and measuring conditions. Initial rapid decrease can be result of shear-induced breakdown of the internal structure of the material. The rate and extent of viscosity reduction depend on both the applied shear rate and the resting time. The effect of resting time on the time-dependent flow properties of yolk is presented in Fig. 9. At constant shear rate,

the apparent viscosity of yolk increases with increasing resting time. There is no significant difference between viscosity values of fresh (0 days in rest) and 1 day in rest yolk, but additional resting changes (increases) viscosity considerably. This effect could be explained as a mutual reaction between air oxygen and yolk matter. Approximate difference in viscosity value between fresh yolk and 3 days resting one ranges about 25%.

Continuing reduction of viscosity value visible in Fig. 8 and absence of equilibrium state (common at lower share rates) can be explained as an influence of sample heating in experimental device as a consequence of rather high share rate. Authors suppose that in case of completion of measuring device with thermoregulator, equilibrium state effect would appear even at this share rate. This problem is also solved in literature (Abu-Jdayil, 2001).



8: Experimental and modelled time-dependant behaviour of RIR yolk



9: Time-dependant behaviour of BPR yolk and differences between fresh and rested material

Also time-dependant behaviour was modelled using similar procedure as in previous case. Two simple models of following form were applied:

$$\eta = a \exp(bt) + c \exp(dt), \quad (7)$$

where: $a = 247.6$ $b = -0.00115$ $c = 1164$ $d = 0.000002569$ $R^2 = 0.9893$.

$$\eta = at^b + c, \quad (8)$$

where: $a = 3790$ $b = -0.01684$ $c = -2130$ $R^2 = 0.8991$.

Again, the exponential fitting (7) with $R^2 = 0.9893$ showed the best match with experimental data. Proposed simple model could be used for predicting yolk behaviour loaded at similar conditions.

CONCLUSIONS

Experiments were performed on egg yolk to investigate the effect of hen breed, storage conditions and resting time on its flow behaviour. The eggs were stored at different temperatures (from 4 °C to 16 °C) for different time periods up to 8 weeks. The samples were shared at different rates (0.34 – 68 s⁻¹) and sha-

red for rather long times – up to 7000 s. Some samples were left to rest at room temperature for 1, 2, 3 and 4 days and the changes in viscosity were monitored. No difference between rheological behaviour of two examined hen breeds were statistically provable. Yolk exhibited shear-thinning and thixotropic behaviour regardless of the storage time or temperature. At constant shear rate, the apparent viscosity of yolk decreased with storage time. The pH of yolk was changed (with a little variation) from 5.90 (fresh egg) to 6.25 (8 weeks of storing). This increase is caused by concentrate of ammonia created from protein during ageing. Increasing storage temperature also decreases the viscosity value. The value of viscosity measured after 8 weeks of storing at 16 °C reached only 21% of viscosity of fresh sample. On the contrary, resting the sample at room temperature in open container increased viscosity value. The value after three-day rest increased for 25%. The time-dependant viscosity decreased rapidly with time and at lower share rates reached an equilibrium stage. The time-dependant viscosity was also found to decrease with storage time.

The non-Newtonian behaviour of yolk as well as time-dependant behaviour was modelled using simple models. The exponential fitting exhibited generally the best results.

SOUHRN

Reologické vlastnosti vaječného žloutku

Práce je součástí rozsáhlejšího projektu sledování reologických vlastností různých biologických materiálů a potravin. Zde jsou prezentovány výsledky sledování reologického chování vaječných žloutků v závislosti na délce a teplotě skladování, rychlosti a trvání deformace a délce odležení vzorku při pokojových podmínkách.

Sledována byla vejce dvou hnědovaječných snáškových plemen (plymutky žíhané a rodajlendky červené). Vejce byla skladována při rozdílných teplotách: 4 °C, 8 °C, 12 °C a 16 °C za konstantních podmínek po dobu 0, 1, 2, 3, 4 a 8 týdnů. Po uplynutí doby skladování byly z vajec připraveny výše popsanou metodou vzorky žloutků. Některé vzorky byly dále ponechány v otevřené nádobě při pokojové teplotě po dobu 1, 2 a 3 dnů.

Nebyla zjištěna žádná statisticky prokazatelná korelace mezi reologickými vlastnostmi žloutků a plemenem nosnic. Určitým způsobem problematickým bodem zůstává příprava vzorku a naměřené hodnoty jsou prezentovatelné jako výsledky měření žloutkové rozmíchané hmoty.

Žloutek vykazoval známky „shear-thinning“ a tixotropie bez ohledu na délku nebo teplotu skladování. Hodnota pH se s dobou skladování zvyšovala. S malými odchylkami se hodnota pH pohybovala od 5,90 (čerstvý materiál) po 6,25 (8 týdnů skladování). Při shodné rychlosti deformace docházelo k poklesu hodnot viskozity žloutku s délkou skladování. Zvyšující se teplota skladování taktéž tuto hodnotu snižovala. Hodnota viskozity po 8 týdnech skladování při 16 °C dosáhla pouze 21 % hodnoty viskozity čerstvého vzorku. Naopak odležení vzorku v otevřené nádobě při pokojové teplotě viskozitu vzorku zvyšovalo. Po třídním odležení byla viskozita vyšší o 25 %.

Dále byla sledováno časově závislé chování vzorků. Viskozita rychle klesala s časem zatěžování a u nižších rychlostí deformace dosáhla vyrovnaného stavu. Také u časově závislé viskozity byl zjištěn pokles s délkou skladování. Ne-newtonovské chování žloutku a časové závislosti viskozity byly modelovány pomocí jednoduchých modelů. Bylo dosaženo uspokojivých výsledků s vysokými korelačními koeficienty.

vaječný žloutek, reologické vlastnosti, viskozita, rychlost deformace, pH, modelování

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