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Permeability of gels is set by the impulse applied on the gel

V. Urbonaite [a, b, *], H.H.J. de Jongh [a, c], E. van der Linden [a, b], L. Pouvreau [a, d]

[a] Top Institute Food & Nutrition (TIFN), PO Box 557, 6700 AN Wageningen, The Netherlands
[b] Laboratory of Physics and Physical Chemistry of Foods, Department of Agrotechnology and Food Sciences, Wageningen University, P.O. Box 17, 6700 AA Wageningen, The Netherlands
[c] ProtIn Consultancy, Nepveulaan 112, 3705LG Zeist, The Netherlands
[d] NIZO Food Research, PO Box 20, 6710 BA Ede, The Netherlands

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ABSTRACT

To better understand sensory perception of foods, water exudation studies on protein-based gels are of a high importance. It was aimed to study the interplay of gel coarseness and gel stiffness on water holding (WH) and water flow kinetics from the gel once force is applied onto the material. Ovalbumin heat-set gels were used as a model system, where protein volume fraction was kept constant and ionic strength was varied to obtain a range of different gel morphologies and stiffness. WH of gels was measured both as a function of time and force applied. From experimental data (i) an effective gel permeability coefficient and (ii) an effective water flux coefficient were obtained and related to gel coarseness and stiffness. Gel coarseness determined maximum amount of water removed from the gel at defined conditions, where lower (≤0.1 μm) and upper (≥0.4 μm) limiting scales for water removal were identified. Gel stiffness is the major determinant for water removal kinetics from the gel. The combination of gel coarseness and gel stiffness showed a cooperative effect on gel WH. The insights can be exploited in product development to predict and tune oral perception properties of (new) products.

1. Introduction

To better understand sensory perception of foods, water exudation studies on protein-based gels are of a high importance. The water holding (WH) property of a gel is determined by gel characteristics (Hermansson & Lucisano, 1982; Urbonaite, de Jongh, van der Linden, & Pouvreau, 2014, 2015). First, the microstructural (morphological) aspects of the gel network appear to be relevant. Secondly, deformability of the network by an applied force affects water exudation from the gel.

The morphological aspects of the gel network are set by e.g. the type of protein, its concentration, the pH, ionic strength and type of salts present (Foegeding, Bowland, & Hardin, 1995; Hermansson, 2008; Maltais, Remondetto, Gonzalez, & Subirade, 2005; Molina, Defaye, & Ledward, 2002; Renkema & van Vliet, 2002). The impact of morphology on WH capacity has been reported for different protein systems and attempts to link it to typical length scales in the network have been made (Chantrapornchai & McClements, 2002; Hermansson, 1982; Puppo & Añón, 1998; Puppo, Lupano, & Anon, 1995; Stevenson, Dykstra, & Lanier, 2013; Urbonaite et al., 2014, 2015). It has been reported that pore size diameters in the range of 0.1–2 μm are relevant for WH (Hermansson, 1986). More recently, the water loss of soy protein gels was reported to be most sensitive in the pore size range of 0.3–4.7 μm (Urbonaite, de Jongh, van der Linden, & Pouvreau, 2015).

The extent the gel structure deforms upon applied force is crucial for exudation of water (Hermansson, 2008). Van den Berg and colleagues showed that serum flow rate from the gel was a direct function of the network porosity and was higher at higher compression rates (van den Berg, van Vliet, van der Linden, van Boekel, & van de Velde, 2007). Urbonaite et al. showed that gel stiffness was related to WH property in soy protein gels, were stiff gels had low WH and less stiff gels had high WH (Urbonaite et al., 2014).

Once a single protein gel system obtained by e.g. varying pH or salt concentration is studied, typically gel coarseness is dominant in determining WH (Urbonaite et al., 2015). However, when two different protein systems differing in protein source or processing condition are compared, gels comparable in apparent coarseness may result in different WH. This suggests that gel microstructure is

* Corresponding author. TI Food and Nutrition, P.O. Box 557, 6700 AN Wageningen, The Netherlands. Tel.: +31 317 486160.
E-mail address: vaida.urbonaite@wur.nl (V. Urbonaite).

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not a single determinant in WH property. Gel coarseness and stiffness parameters are interrelated, but thus far to our knowledge no attempt to dissection the effect of gel coarseness and gel stiffness on gel WH under applied pressure was reported.

When water transport mechanisms in relation to gel coarseness are studied, in most studies network stiffness and time- or force-dependent changes in the gel morphology are not taken into account. Water transport simulations in porous media based on Darcy's law are applicable only for laminar flow in solid non-deformable porous medium (Walstra, 2003). Such analysis leads to permeability coefficients reflecting gel coarseness (Mellema, Heesakkers, van Opheusden, & van Vliet, 2000; Verheul & Roefs, 1998). In relation to coarseness Hermansson (2008) proposed three different length scale-dependent water transport mechanisms in the gel: (i) hydrodynamic flow, (ii) capillary flow and (iii) molecular diffusion (Hermansson, 2008). Hydrodynamic and capillary flows are apparent on macro-to micron scales. Hydrodynamic flow is active in large and open structures, and is driven by gravity or external forces. Capillary flow depends also on surface tension of the liquid, where an external pressure higher than capillary pressure is needed to displace water (Hermansson, 2008; Stevenson et al., 2013). Molecular diffusion is apparent on nanometer scale and is more of importance for the mass transport of molecules or small particles in the gel matrix rather than for WH.

To measure hydrodynamic and capillary flow, an external force has to be applied. The measurement of WH comprises two distinct aspects: (i) the maximum amount of water that is exuded from the protein gel, at a given force, and (ii) the kinetics of this exudation, or as often referred to, the 'ease of flow' (Kocher & Foegeding, 1993). In this work we aim to show how gel coarseness, defined as microstructure inhomogeneity, and gel stiffness affect water flow from the gel under applied force. As a model system for this study ovalbumin heat-set gels were used. Ovalbumin, as the main protein in egg white, is highly relevant for the food industry for a range of applications, and is well-studied for its aggregation and gelation mechanisms (Weijers, Visschers, & Nicolai, 2004). The approach was taken to have a constant protein volume fraction and to vary ionic strength to obtain a range of different gel morphologies. Obtained gels are then analyzed for their coarseness using image analysis of CLSM and SEM images, their stiffness using large deformation rheology, and WH capacity measured by centrifugation in time over a range of forces applied or at constant forces applied as a function of time.

2. Material and methods

2.1. Material

Ovalbumin was purchased from Neova (lot no: BB13191, Abbotsford BC, Canada) with a purity of 90%. Sodium chloride (NaCl) was obtained from Sigma–Aldrich (Steinheim, Germany). Reagents were of analytical grade and used without further purification.

2.2. Preparation of gels

Ovalbumin was dissolved in milliQ water to 12% (w/w) protein at pH 7.5. The protein solution was mixed with different concentrations of NaCl. The protein solution prior to gelling was de-aerated under vacuum for 5 min (vacuum pump MZ 2C NT, Vacuubrand, Wertheim, Germany). Gelation was performed in 20 ml syringes (20 mm in diameter), lubricated with paraffin oil, and closed airtight to reduce air bubble formation during heating the samples at 95 °C for 20 min in a water bath and subsequently cooling overnight at room temperature. Every sample was prepared at least in duplicate.

2.3. WH measurements at given time and pressure

The centrifugation procedure of gels was adapted from Kocher and Foegeding (Kocher & Foegeding, 1993). A microcentrifuge filtration unit was composed of an inner spin tube and a 2 ml Eppendof tube (Axygen Biosciences, Inc., Union City, USA). Gels were cut in 10 mm high and 4.8 mm diameter cylinders using a cork borer and carefully placed on the bottom of the spin tube. The bottom of the spin tube was covered with a 5.5 mm diameter filter paper to reduce grid size. Centrifugation was performed at 20–1000 relative centrifugal forces (RCF) for 10–40 min at 20 °C. Expulsed serum from the gel was collected at the bottom of the Eppendorf tube. The WH was defined as the percentage of water in the gel remaining after centrifugation according to

$$WH = \frac{W_T - W_{RCF}}{W_T} \cdot 100 \quad [\%] \tag{1}$$

where W_T is the total amount of water in the sample and W_{RCF} denotes the amount of water removed from the sample at a given RCF. Measurements were performed in duplicate.

To evaluate the magnitude of pressure applied on the gel RCF was converted to applied pressure (P) in Pascal (Pa) as follows:

$$P = \frac{\left(V_s \cdot \varnothing_{protein} \cdot \rho_{protein} + V_s \cdot \varnothing_{water} \cdot \rho_{water}\right) \cdot RCF \cdot g}{A} \tag{2}$$

where Vs is volume of the sample (m^3),$\varnothing$ is volume fraction of proteins or water in the sample, ρ_{prot} = 1350 kg/m^3 (Fischer, Polikarpov, & Craievich, 2004), g is gravitational acceleration (9.8 m/s^2), and A is area of the cylinder top surface (m^2). As an example, 100 RCF is equivalent to 10 kPa applied on the gel. Water removed from the sample is expected to be proportional to applied force, which would hold for a specific time of centrifugation. Using above described experimental set-up WH of gels was measured (i) as a function of applied pressure (P), when the time was fixed (e.g. gels centrifuged at 20–1000 RCF for 1 min, 2 min, 3 min and etc. up to 40 min), and (ii) as a function of time (t), when the pressure was fixed (e.g. gels centrifuged at 1–40 min at 20 RCF, 50 RCF, 100 RCF and etc. up to 1000 RCF). Obtained WH data versus applied pressure (P) at fixed times, and time (t) at fixed applied pressures were fitted using Equation (3) assuming a single exponential decay

$$WH = A \cdot exp^{-k_i f(P,t)} + B \tag{3}$$

from where the fitting parameters A, the maximum percentage of water which can leave the system, further denoted as A_{max}, B, percentage of water remaining in the gel, and k_i, kinetics parameter either as a function of applied pressure or time were determined. Fitting parameter k as a function of pressure at fixed different times was denoted as k1 and reflects effective gel permeability coefficient change over time. Parameter k as a function of time at fixed different applied pressures was denoted as k2 and reflects water flux coefficient from the gel change over applied pressure. Fitting the curves (using Origin60) assuming two exponential decay functions did not yield a significant improvement of the fit. Change in k2 slope was calculated using Excel slope function between second and third points of each curve. Calculated values of the initial slope depended on the pressure-interval chosen. However, independent of the pressure where the differences were analyzed, the outcome and conclusive lines were similar.