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Deformation and fracture behavior of physical gelatin gel systems

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ABSTRACT

Food scientists usually used biopolymer physical gels as model systems because they are structurally and mechanically similar to many gel-like food products. In this paper, eight gelatin gel systems with different stiffness were prepared by varying gelatin concentration (10–30%w/w), collagen source (bovine/porcine) and solvent composition (0/40%w/w glycerol/buffer mixture). The swelling behavior was evaluated and the mechanical response was characterized through puncture tests, uniaxial compression experiments and wire cutting fracture tests. From these tests, apparent gel strength, first order Ogden constitutive parameters (shear modulus, μ, and strain hardening capability, α) and fracture toughness (G_c) were determined. Samples that display apparent gel strength and swelling behavior consistent with a more physically cross-linked structure exhibit larger μ and G_c and lower α values. It is shown that α and G_c are related with μ independently of gelatin concentration, collagen source and glycerol presence. α decreases exponentially with increasing μ whereas G_c increases linearly with μ. The found experimental trends suggest that in the quasi-static range the overall mechanical behavior of gelatin gel systems is mainly controlled by the initial shear modulus, which is a direct measure of gel stiffness.

1. Introduction

Determination of mechanical properties is of great importance for food scientists and technologists since the mechanical response affects food processing, handling and consumption. On one hand, during manufacturing, food products are subjected to large strains that may cause severe deformation or even final fracture, affecting their structural integrity. On the other hand, large deformations and fracture processes are involved in biting and mastication and therefore, they are linked to consumer's acceptance and preference. It has been shown that large deformation properties are associated to texture perception and display good correlation with sensory evaluation (Barrangou, Drake, Daubert, & Foegeding, 2006a; Foegeding, Brown, Drake, & Daubert, 2003; Foegeding, 2007; Foegeding et al., 2011; Takahashi, Hayakawa, Kumagai, Akiyama, & Kohyama, 2009).

The structure of many foods, such as processed meats, cheese, gelatin desserts, cooked egg whites, frankfurters, surimi based seafood analogs, yogurt and confectionery products, is dependent on the formation of a gel network. Due to the high complexity of these foods, biopolymer gels are commonly adopted as model systems for mechanical investigations (Barrangou et al., 2006a, b; Foegeding & Daubert, 2008; Sala, 2007). Among biopolymer gels, physical gelatin gels are interesting materials since their stiffness can be easily manipulated. In these gels, the network is composed by ordered triple-helix (rigid) segments stabilized by intermolecular hydrogen bonds, which resembles the nature collagen state, interconnected by flexible protein chains that remain in the coil conformation (Joly-Duhamel, Hellio, Ajdari, & Djabourov, 2006a). The collagen-type triple helices act as the physical crosslinking points of the gel network. Gels containing large amounts of triple-helices are strongly cross-linked and become rigid (Bigi, Panzavolta, & Rubini, 2004; Joly-Duhamel et al., 2006a). The amount of triple helices in gelatin hydrogels depends on gelatin concentration,

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thermal treatment and amino-acid composition (Joly-Duhamel et at., 2006a). In addition, the presence of sugars and other polyols enhances the formation of triple helices due to a preferential hydration effect. It is known that low molecular weight carbohydrates bind water in their hydration shells enhancing protein–protein interaction and thus helix formation (Joly-Duhamel, Hellio, Ajdari, & Djabourov, 2006b; Sanwlani, Kumar, & Bohidar, 2011; Seishi & Matubayasi, 2014). Therefore, gelatin gel stiffness can be tailored through proper selection of these variables.

Determining true mechanical properties of biopolymer gels is not a simple task due to its low modulus (of the order of 1–100 kPa) and inherent complex mechanical behavior. Biopolymer gels are soft materials that support large deformations and show strain hardening, resembling the hyperelastic behavior of elastomers. However, these materials exhibit brittle fracture, which is highly dependent on strain rate (Bot, van Amerongen, Groot, Hoekstra, & Agterof, 1996; Czerner, Martucci, Fasce, Ruseckaite, & Frontini, 2013; Forte, D'Amico, Charalambides, Dini, & Williams, 2015; Gamonpilas, Charalambides, & Williams, 2009; Urayama, Taoka, Nakamura, & Takigawa, 2008). The fracture mechanism in biopolymer physical gels has been explained as a viscoplastic pull-out process of the chains that constitutes the network, which is different to the typical chain scission mechanism that occurs in chemical gels (Baumberger, Caroli, & Martina, 2006).

The puncture test is probably the most popular mechanical test used to measure textural properties of soft foods (Chen & Opara, 2013). As well, this test can be applied to determine the gel strength of gels (Chiou et al., 2006). A punch of defined geometry is pushed into the gel sample up to a selected depth, and the recorded load is the technical term gel strength. A particular case of this measurement is the so-called Bloom test extensively adopted to assess the grade and quality of a gelatin. It should be considered that this type of single point measurements is not completely representative of the large deformation behavior of gels. In an own previous work, it was shown that a wide variety of gelatin gels display strain hardening at deformations larger than those imposed in the puncture test (Sanchez Fellay, Fasce, Czerner, & Frontini, 2015).

A more complete description of the large deformation behavior of gels can be carried out by uniaxial compression tests (Christianson, Casiraghi, & Bagley, 1986; Forte et al., 2015; Gamonpilas et al., 2009; Miller, 2005; Takahashi et al., 2009). In this test, a cylindrical sample is compressed while the load and displacement are continuously registered. The stress–strain relationship can be directly obtained from the measured data and interpreted by proper constitutive models to obtain intrinsic material parameters. The Ogden constitutive model has been widely adopted to describe the hyperelastic behavior of soft materials including hydrogels and living tissues under uniaxial compression (Comley & Fleck, 2012; Gamonpilas et al., 2009; Rashid, Destrade, & Gilchrist, 2012; Sasson, Patchornik, Eliasy, Robinson, & Haj-Ali, 2012; Sparrey & Keaveny, 2011).

Regarding fracture characterization, different test configurations such as single edge bending, tear, constrained tension and wire cutting were proposed in the past to evaluate the fracture toughness of gels (Baumberger et al., 2006; Chen & Opara, 2013; Czerner, Fasce, & Frontini, 2014; Gamonpilas et al., 2009; Kamyab, Charalambides, & Williams, 1998; Luyten, Vanvliet, & Walstra, 1992). Among these test configurations, the so-called “Wire Cutting method” is very attractive due to its simplicity. It involves pushing wires of different diameters into a specimen to promote a steady state cutting process, while the load and the wire advance are recorded. The crack propagation rate is directly the imposed wire displacement rate, in contrast to other test configurations in which it needs to be measured by monitoring the crack length at various time intervals. This method has been used to evaluate the energy release rate, G_c, of chesses (Goh, Charalambides, & Williams, 2005; Kamyab et al., 1998) and physical gels (Czerner et al., 2014; Forte et al., 2015; Gamonpilas et al., 2009). The arisen fracture toughness parameters were shown to be in agreement with those obtained by using more complex techniques. In particular for gelatin gels, consistent fracture toughness parameters have been determined provided that a flattened surface fracture pattern is developed during the test (Czerner et al., 2014).

In this work, gelatin gel systems displaying different stiffness were prepared. The investigation was conducted in order to analyze the relationships between stiffness and large strain and fracture parameters of physical gels. For this purpose, formulation variables, such as powder concentration, gelatin source and solvent composition, were intentionally varied to promote the formation of gels with different triple helix content and hence with different stiffness. Gel systems were subjected to puncture and uniaxial compression tests and to wire cutting fracture experiments. Mechanical parameters were determined and then interpreted in terms of the gel physical structure. This research pretends to provide deeper insight and knowledge on how gel stiffness controls the overall mechanical behavior of gel-like foods.

2. Materials and methods

2.1. Gelatin gels preparation

Two commercial lyophilized gelatins arisen from different sources were used to prepare gel samples: bovine hide gelatin (Type B, Bloom 200, isoelectric point 4.7–5.4) and pork skin gelatin (Type A, Bloom 250, isoelectric point 7–9), both kindly supplied by Rousselot Argentina. Phosphate buffer solution (pH 7) and borate buffer solution (pH 10) were used as solvents to obtain hydrogels. A 40%w/w glycerol/buffer solution was used to prepare mixed solvent gels. All chemicals were of analytical grade (Ciccarelli).

Gel-forming solutions were obtained by dissolving gelatin in the solvent at different concentrations varying from 10 to 30%w/w. Solutions were homogenized under mild stirring for 15 min at 50 °C. For each gelatinsource type, the pH of the solvent was selected over the isoelectric point to obtain anionic polyelectrolytes gels. Gelatin solutions were poured into cylindrical Delrin® molds and cooled at room temperature to form the gels. Gel samples were wrapped in polyethylene film to minimize loss of water and stored at 4 °C during 48 h before testing.

Details of gels formulations are given in Table 1. Gel density values reported in Table 1 were measured by pycnometry and used to calculate the actual gelatin concentration (C_{gel}) in the gels.

2.2. Swelling experiments

Gels used for swelling studies were first lyophilized for 48 h to obtain dried samples. After dehydration, samples were accurately weighed and immersed in 20 ml of distilled water at 20 ± 2 °C until the swelling equilibrium was achieved (Qiao & Cao, 2014). At regular intervals of time, samples were taken out from the distilled water, blotted using absorbent paper and weighed. The Swelling Ratio (*SW%*) was calculated at each time point from the dried sample weight (W_d) and the swollen sample weight at time t (W_t), as:

$$SW\% = \frac{(W_t - W_d)}{W_d} \times 100 \quad (1)$$

The Equilibrium Swelling Ratio (*ESR*) was calculated as (Qiao & Cao, 2014):