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Modulation of extruded collagen films by the addition of co-gelling proteins

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ABSTRACT

Collagen can be modified by the addition of co-gelling proteins. The extrusion of these gels might lead to collagen films with new functionalities, e.g. microstructure and texture. An amount of 4% (w/w), 2.75% (w/w) telopeptide-poor or native collagen and 2.75% (w/w) of both collagen types containing 1.25% (w/w) soy protein isolate, blood plasma or gluten were extruded utilizing a laboratory nozzle extruder system to form films. Gels and films were analyzed using rheology, tensile tests and microscopy. Results indicated that co-gelling proteins are more prone to incorporation in highly crosslinked native collagen gels, as indicated by a maximal consistency index k^* of 2.00 10^{-3} Pa s^{-n^*}, rather than cluster-like telopeptide-poor collagen gels, as indicated by a maximal consistency index value of 0.50 10^{-3} Pa s^{-n^*}. However, the film forming ability of collagen could not be matched by any other protein, as shown by decreased complex viscosities when co-gelling proteins were added. The addition of gluten to telopeptide-poor collagen impaired the film strength due to phase separation leading to lumps. Both collagen types featured comparable tensile strengths, ranging from 0.42 to 1.70 kPa, suggesting that the ionic bonds caused by precipitation determine the film strength, rather than initial covalent crosslinks. The 4% (w/w) pure collagen gels of either type yielded the thinnest films, however, with the highest tensile strength and complex viscosity. Results thus suggest that addition of co-gelling proteins presents a suitable approach to modify the gel strength in order to create collagen films with altered elasticity or tensile strength, leading to sausages with modified sensory attributes, e.g. bite or snap.

1. Introduction

The world consumption of meat and meat products has increased immensely over the last couple of years, and shortage of raw materials is increasingly an issue. Therefore, the continuous production of co-extruded sausages using collagen has greatly increased, since it eliminates the need to use one of the most costly and scarce raw materials in meat product manufacturing, i.e. natural casings (Barbut, 2010). Fibril forming collagens are very well suited to the production of edible sausage casings, since they form readily stable networks that are able to shrink and stretch to accommodate contraction and expansion of meat batter during continuous processing (Osburn, 2002). However, there is little research data published that has focused on the physicochemical properties of collagen formulations and their impact on the mechanical properties of the extruded or co-extruded casings (Harper et al., 2012).

In general, extrusion has been defined as 'the act or process of shaping a material by forcing through a die' (Merriam-Webster, 2008). Collagen extrusion technology was initially developed in the packaging and meat industry, where it was used to generate edible food casings from bovine or porcine skin-derived collagen fibers (Hoogenkamp et al., 2015). In the co-extrusion process, the collagen gel is extruded simultaneously with the sausage emulsion

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in either a rotating cone or a counter-rotating nozzle apparatus. The rotation causes the collagen fibers to align into an oriented structure. There, film strength and elasticity can be adjusted by the inner and outer rotational speed of the cones (Embuscado and Huber, 2009; Hoogenkamp et al., 2015; Lieberman, 1964). A lower rotational cone speed leads to films with higher tensile strength and elasticity due to a more random orientation and a higher degree of entanglement of collagen fibers (Hoogenkamp et al., 2015). Exiting the nozzle, the collagen film is precipitated and dehydrated in brine solution, such as a saturated sodium chloride solution, yielding a dense collagen network with higher tensile strength (Anonymous, 2005; Harper et al., 2013; Kalle, 2010; Shulman et al., 2007). A subsequent treatment with glutaraldehyde, glyoxal, liquid smoke, sugars, or mineral tanning agents facilitates chemical crosslinking and further film stabilization (Cohly and Turbak, 1974; Harper et al., 2013; Morgan et al., 1998). Using bovine or porcine collagen, semi-dried sausages, fresh sausages such as 'bratwurst', or breakfast sausages can be fabricated (Anonymous, 2005). Here, the use of alternative film-forming protein sources would open new markets. For instance, collagen from chicken meat by-products (skin, bone cartilage) may not only allow for the production of conventional sausage, but may also facilitate the production of halal or kosher ones. Collagen obtained from different animal species may also feature different gel properties, yielding films with different functionalities (e.g. stretchability, optical appearance, bite). This may for example be ascribed to differences in animal age upon slaughter, since the number of covalent crosslinks increase with increasing age (Joseph, 2003; Maurer, 2003). Consequently, collagen from different species or younger animals might have varying properties, and thus perform differently in a co-extrusion process. Moreover, modifications in pH and ionic strength, as well as the addition of Hofmeister anions or co-gelling proteins have shown to lead to changes in collagen gel properties (Oechsle et al., 2015a, b; Oechsle et al., 2014). While this has led to advances in the understanding of gels manufactured from more or less crosslinked collagen gels modified by addition of co-gelling proteins, pH and salt addition, relatively, little is known as to the properties of extruded and precipitated films formed from such gels.

The aim of this study was therefore to investigate in a first step the impact of a substitution of native and telopeptide-poor collagen by co-gelling proteins and investigate the properties of extruded and precipitated films. With exception of whey protein isolate, which had decreased collagen viscosity so much so that extrusion was not feasible, all co-gelling proteins investigated in our previous study (Oechsle et al., 2015a) were utilized. Thus, soy protein isolate, blood plasma protein, and gluten were applied as co-gelling agents. Moreover, a highly crosslinked native collagen and a marginally crosslinked telopeptide-poor collagen, consisting of single triple helical tropocollagen molecules, were used in order to gain insights into the influence of the number of initial crosslinks being present in a collagen matrix. Hence, telopeptide-poor collagen can also be seen as a model system for less crosslinked samples, such as chicken collagen and therefore it may also serve as chicken analogue to gain further origin related insights into collagen. To that purpose the rheology of gels as well as the rheology, tensile strength, and microstructure of the extruded and precipitated films were investigated.

In this context, it was hypothesized that native collagen containing co-gelling proteins might lead to stronger films than telopeptide-poor collagen, due to the presence of covalent crosslinks leading to a well entangled gel network. By contrast, telopeptide-poor collagen, which was found to yield cluster-like structures (Oechsle et al., 2014), might profit less from the addition of co-gelling proteins. Thus, strengthening or weakening effects may be more distinct for telopeptide-poor collagen. According to the findings of our previous study (Oechsle et al., 2015a), the substitution of telopeptide-poor collagen by soy protein isolate might lead to stronger films, due to the formation of additional strands within the collagen pores. The use of blood plasma protein might not contribute to an increase of the tensile strength based on neither strengthening nor weakening effects in the gel. By contrast, the substitution of collagen by gluten, promoting phase separation, might deteriorate the tensile strength and elasticity of the extruded films.

2. Materials and methods

2.1. Preparation of collagen gels

Bovine native collagen was kindly provided by Kalle GmbH (Wiesbaden, Germany). Bovine telopeptide-poor collagen was obtained from Protein Consulting (Singhofen, Germany) by splitting off telopeptides and intermolecular crosslinks from native collagen to obtain single collagen triple helices (Büker et al., 2010). Both samples were found to be of collagen type I in our former work (Oechsle et al., 2014). There, telopeptide-poor collagen was used as a model system to elucidate effects for less crosslinked collagen types. A total protein concentration of 4% (w/w) was chosen, due to its use in the industry and favorable gel properties with respect to extrusion. For the mixed gels, 1.25% (w/w) collagen was substituted by co-gelling proteins, namely soy protein isolate (PRO-FAM 974, ADM Specialty Products-Oilseeds, Decatur, IL, USA), blood plasma protein (Tastemakers GmbH, Stuttgart, Germany) and gluten (Hermann Kröner GmbH, Ibbenbüren, Germany (Oechsle et al., 2015a). A concentration of 1.25% (w/w) co-gelling protein in the mixed gels was selected, since preliminary studies had shown that both weakening and strengthening effects were evident, and the weakest gel was still viscous enough to allow being extruded. The co-gelling proteins were added to the collagen concentrates, diluted with double distilled water and homogenized, using the lowest mixing speed in a bowl chopper KP4DCM VAK (Seydelmann KG, Aalen, Germany) for 5 min. The pH was adjusted to pH 3 with phosphoric acid (ChemSolute, Renningen, Germany) while mixing. The choice of pH was based on results of our previous study (Oechsle et al., 2014) showing that under these conditions entanglement was maximal. Finally, the gels were evacuated for 20 min at 85% vacuum in the bowl chopper.

2.2. Preparation of the collagen films

Fig. 1 depicts the laboratory nozzle extruder system. Collagen gels were extruded through a rotational nozzle at $n = 65$ rpm, $V = 2$ L min^{-1} and with a gap width of 0.1 mm using a vane pump (VF 80/165-1, Handtmann, Biberach, Germany). Consequently, the films were precipitated with a saturated sodium chloride solution at 5 °C directly at the outlet of the circular slit nozzle. Precipitation occurs, due to the salt withdrawing water from the collagen matrix leading to salting out and stable, firm films.

2.3. Rheological measurements

Experiments were conducted in a modular compact rheometer, Physica MCR 502 (Anton Paar, Ostfildern, Germany), at 5 °C using a plate–plate geometry PP25/S with 24.98 mm diameter and a sandblasted surface to avoid wall-slip (Anton Paar, Ostfildern, Germany). Collagen gels and films of telopeptide-poor and native collagen were analyzed by rheological measurements. Strain sweeps were performed at 1 Hz in order to determine the linear viscoelastic range determined by the software Rheoplus/32 V3.62