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Viscoelastic properties of soy protein isolate - pectin blends: Richer than those of a simple composite material

Birgit L. Dekkers, Remko M. Boom, Atze Jan van der Goot*

Food Process Engineering, Wageningen University, Wageningen, The Netherlands

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ABSTRACT

Concentrated soy protein isolate (SPI) – pectin blends acquire fibrous textures by shear-induced structuring while heating. The objective of this study was to determine the viscoelastic properties of concentrated SPI-pectin blends under similar conditions as during shear-induced structuring, and after cooling. A closed cavity rheometer was used to measure these properties under these conditions. At 140 °C, SPI and pectin had both a lower G^* than the blend of the two and also showed a different behavior in time. Hence, the viscoelastic properties of the blend are richer than those of a simple composite material with stable physical phase properties. In addition, the G'_{pectin} was much lower compared with the G'_{SPI} and $G'_{SPI\text{-}pectin}$ upon cooling, confirming that pectin formed a weak dispersed phase. The results can be explained by considering that the viscoelastic properties of the blend are influenced by thermal degradation of the pectin phase. This degradation leads to: *i*) release of galacturonic acid, *ii*) lowering of the pH, and *iii*) water redistribution from the SPI towards the pectin phase. The relative importance of those effects are evaluated.

1. Introduction

Meat analogs based on plant proteins have the potential to contribute to a more sustainable diet through reducing the actual meat consumption. Meat analogs having a pronounced fibrous structure are known to be most appealing as alternative to meat for consumers (Hoek et al., 2011). Nowadays, high moisture extrusion is mostly used to make these types of meat analogs (Dubey & Bhattacharya, 2015; Osen & Schweiggert-Weisz, 2016). A decade ago, a structuring technology based on simple shear flow deformation was introduced for the development of fibrous proteinaceous structures with a meat-like appearance (Manski, van der Goot, & Boom, 2007). Plant-based biopolymers can be structured into fibers by using a concentrated two-phase system that consists either of two types of protein; soy protein isolate (SPI) and wheat gluten, or of a blend with protein and polysaccharides, which may be naturally present, as in soy protein concentrate (SPC) or assembled in a model system such as a SPI - pectin blend (Cheftel, Kitagawa, & Queguiner, 1992; Dekkers, Hamoen, Boom, & van der Goot, 2018; Dekkers, Nikiforidis & van der Groot et al., 2016; Grabowska et al., 2016; Grabowska, Tekidou, Boom, & van der Goot, 2014; Liu & Hsieh, 2007). Those immiscible biopolymer blends have a multiphase morphology in which the minor phase forms dispersed droplets. Both the dispersed phase droplets and the continuous phase absorb part of the water, and can therefore be described as a water-in-water emulsion. Similarly to regular emulsions, these droplets can coalesce, deform and break up upon shear-induced structuring. Deformation and break-up of droplets depend on the ratio between the external, viscous and internal or interfacial forces (Grace, 1982; Taylor, 1932). For two droplets to coalesce, they should approach each other and then expel the film in between (Elmendorp & Van der Vegt, 1986; Lyu, Bates, & Macosko, 2000). These forces and phenomena are dependent on the viscoelastic properties, the elasticity, and the interfacial tension of the blend (Elmendorp & Van der Vegt, 1986; Verhulst, Cardinaels, Moldenaers, Afkhami, & Renardy, 2009). Hence, determining these properties can contribute to a deeper understanding of fibrous structure formation processes.

Temperature has been shown to be a key process parameter when transforming protein blends into fibrous structures (Akdogan, 1999; Arêas, 1992; Cheftel et al., 1992; Grabowska et al., 2016). Heating results in a lower viscosity, which influences the flow conditions during high moisture extrusion (Osen & Schweiggert-Weisz, 2016). Furthermore, temperature affects protein cross-linking reactions (Arêas, 1992). The temperature was also shown to be a key process parameter when structuring protein-polysaccharide blends, such as soy protein concentrate and SPI - pectin blends, with simple shear flow (Dekkers, Nikiforidis et al., 2016; Grabowska et al., 2016). Distinct differences in both the micro- and macrostructure were observed when varying the heating temperature between 120 °C and 140 °C during structure

* Corresponding author.
E-mail addresses: birgit.dekkers@wur.nl (B.L. Dekkers), remko.boom@wur.nl (R.M. Boom), atzejan.vandergoot@wur.nl (A.J. van der Goot).

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formation of SPI – pectin blends (Dekkers, Nikiforidis et al., 2016). In this study, these observations on micro- and macrostructure will be connected to the viscoelastic behaviour of the separate components, being SPI and pectin, and the SPI-pectin blend at various temperatures.

In the SPI-pectin blend, the properties of the blend change over time due to chemical and physical instability of both components at elevated temperatures. Pectin is thermally unstable due to non-enzymatic degradation (Chen et al., 2015; Diaz, Anthon, & Barrett, 2007; Shpigelman, Kyomugasho, Christiaens, Van Loey, & Hendrickx, 2014; Thakur, Singh, & Handa, 1997). At neutral pH, β-elimination leads to lowering of the molecular weight. Furthermore, both β-elimination and demethoxylation result in the release of acid groups resulting in lowering of the pH (Axelos & Branger, 1993; Renard & Thibault, 1996; Thakur et al., 1997). Heating of soy protein can induce rearrangement, aggregation, and degradation reactions (Huang, Chang, & Jane, 1999; Kinsella, 1979). These reactions result in differences in the viscoelastic behavior of the two-phases as separate components, and impact the deformability of the two phases during structuring. Secondly, the chemical and physical instabilities can affect the interactions between the two-phases. For example, lowering of the pH of the blend due to β-elimination and demethoxylation affects aggregation of the protein phase. Degradation of the biopolymers also affects the water binding in the network and hence the water distribution between the two biopolymer phases. This is important since the concentration of the polymers in each phase will determine the actual viscosity in the respective, while also the relative volumes of the phases are important in the structure formation (Dekkers, Emin, Boom, & van der Goot, 2018). Lastly, the chemical and physical changes affect the elasticity of the two-phases. The elasticities of both the droplet and the matrix influence the morphology of the dispersed phase. An elastic dispersed phase will result in droplets that are more resistant against droplet break-up under deformation, whereas elastic matrices result in more deformed droplets and a higher break-up rate (Elmendorp & Maalcke, 1985; Lerdwijitjarud, Sirivat, & Larson, 2002).

The objective of this study was to determine the viscoelastic properties of concentrated SPI-pectin blends during and after applying a high temperature and shear treatment. The viscoelastic time-temperature dependency of the blend will be related to phenomena observed in shear-induced structuring, which was shown to yield fibrous structures (Dekkers, Emin, et al., 2018, Dekkers, Hamoen, et al., 2018, Dekkers, Nikiforidis et al., 2016). The rheological properties under process conditions relevant for structuring cannot be studied with traditional rheometers, because of the extreme concentrations and temperatures. We therefore use a device developed for quantifying rubber rheology to determine the viscoelastic properties of concentrated dispersions of SPI and pectin at elevated temperatures over time. This device encloses the material in a cavity; by applying a closure pressure, water evaporation is prevented (Emin & Schuchmann, 2017). A shear treatment is simulated by using high strain and high frequency.

2. Materials & methods

2.1. Materials

Soy protein isolate (SUPRO® 500E IP) was obtained from Solae (St Louis, MO). The isolate contained at least 83.4 wt% protein (N × 5.71). Pectin extracted from citrus peel (HM-pectin P9135, LOT#SLBQ6929V) was obtained from Sigma-Aldrich (Germany). It has a galacturonic acid content of ≥74.0% on a dry basis and contains ≥6.7% methoxy groups. The degree of methyl esterification is around 70% (Yoo, Fishman, Hotchkiss, & Hyeon, 2006). The pH was adjusted using HCl and NaOH, both purchased from Sigma Aldrich (Germany).

2.2. Sample preparation

Samples were prepared by first mixing the dry soy protein isolate (SPI) and/or pectin powder. NaCl was dissolved in the distilled water phase, after which this solution was slowly added to the dry powders followed by mixing shortly. The created blend consisted of 41.8 wt% SPI, 2.2 wt% pectin, 1 wt% salt and 55 wt% water. This ratio between SPI and pectin was used, since we found this ratio to be optimal for shear-induced structuring (Dekkers, Nikiforidis et al., 2016). The separate components consisted of 44 wt% SPI or pectin, 1 wt% salt and 55 wt% water unless stated otherwise. To change the pH of the blend, a NaOH or HCl solution was used instead of water. After mixing, the material was hydrated for at least 30 min.

2.3. Viscoelastic properties

The viscoelastic properties of SPI, pectin, and SPI/pectin blends were determined with a rubber process analyzer (RPA elite, TA instruments, USA), further referred to as a closed cavity rheometer (CCR). The material, approximately 5 g, was placed in between two plastic foils in the closed cavity (disk geometry), which was sealed with a closing pressure of 4.5 bar to prevent water evaporation. Three types of measurements were performed. The first set of experiments consisted of a time-sweep, a cooling step and a frequency sweep. The time-sweep was performed at high strain (80%) and high frequency (10 Hz) while heating at various temperatures (110–140 °C) for 15 min. During the first 30 s, the temperature of the die was lowered due to loading of the samples. Thereafter the set-temperature was reached again (data shown from this point onwards). After the time-sweep, the material was cooled in approximately 12 min from the set temperature to 40 °C by blowing dry air over the disk. Subsequently, the linear viscoelastic regime (LVR) was determined by performing a strain sweep (0.1–100%, 1 Hz), and a frequency-sweep was performed in the LVR (10–0.1 Hz, 1% strain), both at 40 °C. The second set of experiments was used to study the relaxation of materials. Therefore, a time-sweep experiment (80%, 10 Hz) was paused after set time points (2.5, 5, 7.5, 10, 12.5 min), and restarted again after 8 s, for a total of 15 min. The difference in the viscoelastic properties before and after pausing, were determined and used as an indicator for the relaxation behavior of the material. The third set of experiments consisted of time-sweep experiments that were performed for 0.5, 1, 3, 5, 10, and 15 min. The material was cooled down to room temperature in plastic bags to determine the pH of these samples. The gelled materials were grinded and subsequently mixed with distilled water (1:1) to measure the pH.

2.4. Differential scanning calorimetry

Thermal transitions were determined with differential scanning calorimetry (DSC) (Diamond DSC, PerkinElmer, Shelton, USA). The DSC was calibrated with indium, and an empty stainless steel pan was used as reference. Soy protein isolate was dispersed in water (20 wt%). The samples were heated from 20 °C to 150 °C at 10 °C/min and heating cycle was repeated two times. Nitrogen was used as carrier gas. Measurements were analyzed with Start Pyris Software (PerkinElmer, Shelton, USA).

3. Results and discussion

The key question in the first part of this paper is: how do temperature and shear influence the viscoelastic properties of a soy protein isolate (SPI) - pectin blend? First, the viscoelastic properties of separate SPI and pectin were investigated, after which the blends were studied. In these measurements, a high strain and high deformation frequency were applied in a closed cavity rheometer (CCR) to approach process conditions, *i.e.* a shear treatment, that are relevant from an application point of view. Consequently, the measurement is done outside the linear viscoelastic regime (LVR), which means that the resulting periodic stress waveform becomes distorted and deviates from a sinusoidal wave; therefore we refer to apparent G', G'' and G^*-values. After