Effects of flow behaviour and temperature on whey protein gels, pure and in mixture with xanthan

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ABSTRACT
The effects of flow behaviour and temperature on rheological properties and microstructure of particulate whey protein (WPI) gels, pure and in mixture with xanthan, have been investigated. On the laboratory scale, the effects of shear flow at the various states of aggregation for the WPI have been investigated. On the pilot plant, the effects of shear and elongational flow at different temperatures have been investigated in a continuous rotor/stator device.

INTRODUCTION
Biopolymer gels are widely used in various food products, mainly to improve the consistency or to maintain it if the recipe has been changed. As an example, biopolymers are often used to substitute fat in low-fat products, which clearly indicates the high demands on the characteristics of the biopolymers.

During manufacturing, food ingredients become subjected to various process conditions, such as shear forces, stresses, high temperatures and pressure. These conditions often have a large impact on the characteristics of the end product. Therefore, it is important to have a knowledge about the effects of process conditions on the behaviour of biopolymer gels. That would lead to improved food quality and to new product development.

This paper builds on previous published papers by the authors¹⁴. The aim was to receive an increased knowledge about the effects of process conditions on the behaviour of biopolymer gels. Prior to gel formation, the suspensions have been subjected to different flow behaviour and temperatures. The studies have been performed on both the lab- and pilot-plant scale. For simplicity, gels having a history of shear will be denoted shear treated gels.

MATERIALS AND METHODS
The WPI samples¹,³ used were obtained from MD Foods Ingredients, Denmark. The xanthan sample, RHODIGEL®EASY CAS 11138-66-2, was obtained from Meyhall, Switzerland. A detailed description of the materials is given elsewhere¹³. The gels investigated had a pH of 5.4 and a concentration of 10%w/w WPI and 10%w/w WPI+0.1%w/w xanthan, and an added saltconcentration of 0.05M NaCl.

On the laboratory scale, the experiments were performed in rheometers (BOHLIN CS-50, Bohlin Instruments GmbH, Germany, and BOHLIN VOR, Bohlin
Rheology, Chichester, UK), using a couette measuring system. The shearing was performed at different shear rates for various temperature conditions \(^{1–3}\), stated below. On the pilot-plant scale, the suspensions were treated in a continuous rotor/stator device, a shear crystalliser \(^5\) (SC), at different temperatures, rotational speeds and rotor geometries\(^4\). The effects of a defined shear flow in a concentric cylinder system was compared with the shear and elongational flow resulting in a geometry with two scrapers.

Directly after the shear treatments, the WPI was allowed to set under static conditions at 90°C for an hour. The rheological properties of the gels were analysed by dynamic oscillatory measurements. On the laboratory scale, the gel formation was followed by oscillatory measurements in the rheometers stated above\(^1\). On the pilot plant scale, oscillatory measurements were performed on 5mm thick slices of the gels formed, using a parallel plate measuring system. The oscillations were performed with a strain within the linear viscoelastic region and a frequency of 1Hz. The microstructure of the gels was investigated by a light microscope (LM)\(^1\), using the technique of plastic embedding and semi-thin sectioning\(^6\).

RESULTS AND DISCUSSION

**Rheological behaviour**

The effects of shear flow on the laboratory scale on the storage modulus (G’) of pure WPI gels is shown in Fig. 1.

In Fig. 1a, the suspensions have been continuously sheared prior to gel formation, during heating from 20°C up to 76°C, for different rates\(^5\). The shear treatment results in a decreased gel strength, from around 900Pa for the unsheared gel, after an hour at 90°C, to around 200Pa for the shear treated gels. As the rate during the shear increases, the G’ of the gels decreases somewhat\(^5\).

![Figure 1](image-url)

Figure 1. G’ versus time of 10%w/wWPI, pH 5.4. a.) Gel formation at 90°C, after shearing during heating from 20°C to 76°C, b.) G’ during cooling, after shear pulsing. The rate and time for shear pulsing is stated in the legend.

For the WPI/xanthan mixed gels, a shearing during heating from 20°C to 76°C results in a higher or lower G’ compared to that of an unsheared mixed gel, depending on the stress during the shear\(^5\).

In Fig. 1b, the shear has been performed for short times at the gel point, denoted shear-pulsing\(^1\). The changes in G’ upon cooling, after one hour at 90°C, are observed in Fig. 1b. Under a rate of 2.3/s for a time of 15s, the shear-pulsing results in an increased
gel strength, to around 10kPa at 20°C compared to the 6kPa for the unsheared gel. A rate of 92/s for 240s results in a weak gel with a $G'$ of 1.8kPa, suggesting for shear induced aggregate break-up during the shear.

Thus, depending on the aggregation state of the WPI during the shear, the gel strength can be manipulated to show either higher or lower $G'$-values than for an unsheared gel.

The effects on the rheological behaviour of WPI gels of a treatment in the SC (using the rotor geometry without scrapers) is shown in Fig. 2. An oscillatory time sweep of the gels at 20°C is shown. As for the gels continuously sheared on the laboratory scale, the treatment results in a decreased $G'$, from around 10kPa for the unsheared gel to less than 4kPa. The rotational speeds considered are of minor importance for the $G'$-value of the gels, which also agrees with the results found on the laboratory scale in Fig. 1a.

![Figure 2](image)

**Figure 2.** $G'$ versus time at 20°C for 10% w/w WPI gels, pH 5.4. Prior to gel formation, the suspensions were treated in the SC without scrapers at 70°C, for different rotational speeds, see legend.

The complexity of the flow behaviour in the SC increases when introducing scrapers in the geometry. The shear forces increases and vortices and elongational flow appear. For the mixed gels, the effect on $G'$ of a treatment in the SC at 70°C is minor in the absence of scrapers. But, in the presence of scrapers, gels with decreased $G'$ result.

**Microstructure**

The microstructure of unsheared and shear treated WPI gels on the laboratory scale, is shown in Fig. 3.

![Figure 3](image)

**Figure 3.** Network structure of 10% w/WPI gels, pH 5.4. a.) Unsheared gel. b.) Prior to gel formation, continuously sheared at 0.9Pa during heating from 20°C to 76°C, on the laboratory scale.

The structure of the unsheared gel (Fig. 3a) is homogeneous, composed of pores of even size and thin network strands. In contrast, the continuously sheared network (Fig. 3b) is inhomogeneous, composed of thick, dense network regions and different classes of pores. The size of these dense network regions, decreases with an increase in shear rate. For the mixed gels, the continuous shearing results in an increased inhomogeneity in the network structure.

The shear pulsing is of minor importance for the microstructure of the
gels, observed on LM-micrographs\textsuperscript{1,3}. However, when quantifying the pore sizes in the network structures, using image analysis, it was proved however that the shear pulsed networks were more inhomogeneous than the unsheared network.

The effects on the microstructure of a shear treatment in the SC at 70\degree C is shown in Fig. 4, for different rotational speeds.

![Figure 4. Network structure of 10\%w/w WPI gels, pH 5.4. Prior to gel formation, the suspensions were shear treated in the SC, without scrapers, at 70\degree C for a.) 100rpm b.) 900rpm.]

The networks are inhomogeneous and coarse, composed of dense, compact network regions and more loose, sparse network regions. As the rotational speed increases, the dense network regions decreases in size, indicating a sensitivity towards shear forces\textsuperscript{4}. A similar relation between shear rate and dense network regions has been found on the laboratory scale\textsuperscript{1,2,3}.

A comparison between the network structures resulting from the continuous shear on laboratory scale and those resulting from the treatment on pilot-plant scale (Fig. 3b and 4a-b) suggests that it is possible to mimic process conditions on the laboratory scale. The similar rheological behaviour between the gels (Fig. 1a and 2) further support this indication.

![Figure 5. Network structure of 10\%w/w WPI+0.1\%w/w xanthan gels, pH 5.4. Prior to gel formation, the suspensions were shear treated in the SC, with scrapers, at 70\degree C for a.) unsheared mixed gel, b.) 100rpm.]

For the mixed gels, a treatment in the SC prior to gel formation results in an increased inhomogeneity in the network structure. In agreement, this behaviour has also been found from a shear treatment on the laboratory scale\textsuperscript{3}. Furthermore, the changes in flow behaviour accompanying the introduction of scrapers in the SC geometry, has a large effect on the aggregate shape for the mixed gels, see Fig. 5 for unsheared and a SC-treated networks. Rod-like WPI particles appear, which seems to
decrease in size with an increase in rotational speed, see Fig. 5b.

CONCLUSIONS
There are large possibilities to manipulate and control the rheological properties and the microstructure of gels by varying processing conditions, such as shear flow and temperature.
Furthermore, there is good agreement between laboratory scale experiments and pilot-plant experiments, indicating that it is possible to mimic process conditions in a rheometer.

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REFERENCES


