ELSEVIER

Food Hydrocolloids 12 (1998) 459–468

FOOD HYDROCOLLOIDS

Shear-induced structuring of particulate whey protein gels

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Received 15 December 1997; received and accepted in revised form 10 June 1998

Abstract

The effects of steady shear on particulate whey protein isolate (WPI) gels, at pH 5.4, have been investigated by light microscopy (LM) and dynamic oscillatory measurements. The steady shear was performed on suspensions at constant rates between 0.5 and 126/s. The gel point under static conditions (T_g) was around 78 °C and the shearing was performed during heating from 20 to 76 or to 82 °C. The gel point was postponed by the shear up to 82 °C. Steady shear up to 76 °C, at rates less than ~6/s, resulted in a weaker storage modulus (G′), less frequency dependence and a higher stress at fracture compared to the unsheared gel. Steady shear up to 82 °C, at rates below ~6/s, resulted in the formation of two different types of network structure. One structure was similar in appearance to the unsheared network, showing pores in the range of 50 μm. The other structure was dense, composed of smaller particles than the unsheared network and with pores in the range of 10 μm. The gels composed of two structures showed a lower G′ and stress at fracture compared to the unsheared gel. A shear rate above 24/s up to 76 °C resulted in irregular networks, which were composed of two different types of structures. One was loose and open, similar in appearance to the unsheared network structure. The other structure was dense and compact, and was present as individual aggregates. These gels also showed a weaker G′ than the unsheared gel. A shearing up to 82 °C at rates above 24/s resulted in a coarse, inhomogeneous network structure. The gels showed a weak G′, indicating aggregate break-up during the steady shear.

1. Introduction

Industrial processes generally involve rather harsh conditions, such as fluid shear under high temperature and pressure in extruders and pipes. These conditions have a large impact on the characteristics of the products. As most of the products on the market have a process history, it is important to be aware of the relations between product quality and process conditions. The effects of process conditions on cultured milk products, such as yoghurt, have been mimicked by oscillatory shear on casein gels (Arshad, Paulsson, & Dejmek, 1993). The aim of this study was to find the processing conditions under which a cultured milk product could be produced without impairing the structural properties. The study showed that the gel structure gradually broke down under continuous oscillation at high strains. The breakdown was strongly affected by the strain level.

The submission of coarse aggregating polymers to processing conditions generally results in strong effects on both the aggregation behaviour and on the mechanical properties of the samples. Steventon, Donald, & Gladden (1994) studied the effects of fluid shear and process temperature on the aggregation behaviour of whey protein suspensions at pH 6.3. The aggregate growth was found to decrease with increasing shear and the aggregate size increased with temperature. The results indicated that the aggregation process can be controlled by carefully selecting process parameters such as fluid shear and temperature, thus designing the process in order to achieve a preferred aggregation behaviour of the proteins.

The effects of short periods of steady shear in the vicinity of the gel point in particulate whey protein gels, pure and mixed with gelatin, have been studied by Walkenström & Hermansson (1998). It was concluded that it is possible to change the characteristics of both pure and mixed whey protein gels by using controlled shear. Controlled steady shear (approximately 2/s for 20 s) governed the formation of gels, which showed a storage modulus, G′, twice that for an unsheared gel. In relation to the microstructure, the shear treated gels showed more inhomogeneous network structures compared to the unsheared gels. The inhomogeneities were quantified by image analysis at two different magnifications. They revealed that the shear-treated networks

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0268-005X/98/$19.00
PII: S0268-005X(98)00064-2

were composed of different classes of pore sizes at different dimensional levels.

Using the same shear methodology, the effects of steady shear on fine-stranded whey protein gels, pure and mixed with gelatin, have been investigated at pH 7.5 (Walkenström, 1996). Depending on the repulsion in the system, whey proteins have the ability to form two different types of structure (Langton & Hermansson, 1992). In the iso-electric region (roughly between pH 4 and 6), opaque gels are formed with network strand dimensions in the order of μm, denoted particulate gels. At high and low pH-values, transparent gels are formed with network strand dimensions in nm, denoted fine-stranded gels. The effects of short periods of shear in the vicinity of the gel point in fine-stranded whey protein gels proved to be minor (Walkenström, 1996). The microstructure was studied by transmission electron microscopy and the rheological properties by dynamic oscillatory measurements.

From the discussion above it can be concluded that the aggregation behaviour of a polymer and the dimension of the aggregates play a decisive role in the dependence of shear. In relation to this, Walstra & Jenness (1984) suggested that the effects of streaming are dependent on the meeting frequency of particles (J_g), which in its turn is strongly dependent on the particle size. J_g is defined by the relation:

$$J_g = 2/3d^3N^2G$$

where d is the diameter of the sphere, N the number of particles per unit volume and G the velocity gradient (expressed in s^{-1}) (Walstra & Jenness, 1984). The equation shows that the number of collisions of particles is highly dependent upon the particle diameter, $J_g \propto d^3$. Walstra & Jenness (1984) also pointed out that the shear effects depended upon the streaming, which may disrupt floccules and also prevent them from being formed. Furthermore, large flocs are more easily disrupted than small flocs, as they are more likely to have weak spots.

The aim of this study was to extend our knowledge of the effects of processing conditions on whey protein isolate (WPI) gels. Steady shear at constant rates between 0.5 and 126/s was applied on particulate WPI suspensions in a couette measuring system. The flow created in the couette measuring system can be related to that in processes where shear flow dominates. The T_g, gel point under static conditions of the WPI was 78 °C, and the steady shear was performed during heating from 20 to 76 or to 82 °C. After the shear, the suspensions were allowed to set under static conditions. The rheological properties and the microstructure of the gels were investigated by means of dynamic oscillatory measurements and a light microscope, LM.

2. Material and methods

2.1. Material and sample preparation

The whey protein isolate used was obtained from MD Foods Ingredients, named LACPRODAN® DI-9224. It is a commercial product with a protein content of 93%, of which 74% is β-lactoglobulin, 18% α-lactalbumin and 6% bovine serum albumin. The lactose and fat contents were both less than 0.2%. The mineral content is maximum 4%, of which ~0.5% was sodium, ~1% potassium and less than 0.1% calcium.

The WPI powder was dissolved in 0.05 mol/dm^3 NaCl, to a concentration of 10% w/w. The pH-value was adjusted to pH 5.4 at room temperature, using ~0.25 mol/dm^3 HCl.

2.2. Steady shear

The WPI solutions were directly poured into the measuring device of a BOHLIN CS50 rheometer (Bohlin Instruments GmbH, Germany). A couette measuring system was used with a diameter of the bob of 25 mm and of the cup of 27.5 mm. At the start of measurements, the temperature was raised from 20 to 90 °C, using a heating rate of 2.5 °C/min. In order to avoid evaporation and drying effects during the high temperature, silicon oil was added on top of the WPI samples. During the heating from 20 to 76 or to 82 °C, the WPI suspensions were exposed to steady shear. The BOHLIN CS50 was used in the strain-controlled mode, and the steady shear was performed at constant rates between 0.5 and 126/s. Due to the inertia of the bob in relation to the low viscosity of the WPI solutions at the start, it was impossible to perform stable steady shear using a shear rate below 0.5/s. The gel point of unsheared WPI samples, T_g, was determined to be 78 °C by dynamic oscillatory measurements in a strain controlled rheometer, Rheometrics Solids Analyser. The rheometer was equipped with a custom measurement geometry specially designed for shear studies. The oscillations were performed with a strain of 1.5×10^{-3} and at a frequency of 1 Hz.

2.3. Dynamic oscillatory measurements

After the steady shear, the temperature of the samples was increased to 90 °C, at a heating rate of 2.5 °C/min, and kept at this temperature for 1 h, allowing the WPI to set. The gel formation process was monitored by means of dynamic oscillatory measurements, using a strain of 1.5×10^{-3} and a frequency of 1 Hz. The WPI gels were analysed further at 90 °C by frequency sweep and stress sweep. For microstructural analysis, the gels were set further at a controlled cooling rate of 2.5 °C/min. No stress sweep was performed on the gels prepared for microstructural analysis.

2.4. Microscopy

Small pieces of the gels were cut out from the wall of the measuring device. The gap size of the measuring device, 1.25 mm, was taken as the thickness of the gel pieces. The shear rate distribution in the gap was not found to have any effect on the microstructure. The gel pieces were double-fixed in glutaraldehyde and OsO_4. The gels were then dehydrated in a graded ethanol series followed by propylene oxide and embedded in a plastic named Epon. A more thorough description of the microscopy preparation is given by Langton & Hermansson (1992). The gels were cut in 1 μm semi-thin sections, using a glass knife. The sections were stained with toluidine blue and examined under a light microscope, a Zeiss Axioplan.

3. Results and discussion

Steady shear was performed on 10% WPI suspensions, during heating from 20 °C up to various temperatures, chosen in order to affect the WPI in various stages of aggregation. The T_g is around 78 °C and the steady shear was performed up to 76 °C, referred to as $T < T_g$, and 82 °C, referred to as $T > T_g$. When shearing above 78 °C, the gel point is postponed until static conditions prevail. The gels having a history of steady shear will be referred to as "shear-treated gels". The pH-value of the WPI samples was 5.4 and the turbidity of the suspensions, observed as a colour change from more transparent to more opaque solutions, already started to increase at a temperature around 40 °C, indicating aggregation. In agreement with this behaviour, Hermansson (1979) quantified the temperature-induced aggregation of whey proteins by turbidity measurements. It was concluded that the strongest tendency for aggregation of whey proteins is in the vicinity of the iso-electric point (i.p.), which is ~pH 5.2, where a turbidity increase was already found around 40 °C (Hermansson, 1979).

Shearing to a temperature above 82 °C results in an extreme viscosity increase for samples submitted to low shear rates, i.e. less than ~10/s. This viscosity increase is rapid, indicating fast aggregation. An explanation for this behaviour is that the gel point is postponed by the shear, and that the formation of large aggregates is favoured. The gels formed show a very high G′-value, i.e. several kPa at 90 °C compared to ~880 Pa for an unsheared gel. However, the variation in G′ is large for these gels, and furthermore, rheological evidence for slip in the geometry is found. Therefore, no results from shear treatments above 82 °C will be shown.

3.1. Changes in viscosity during steady shear

Changes in the viscosity of the WPI suspensions during steady shear at different rates and increase in temperature are shown in Fig. 1. The viscosity behaviour at rates less than 6/s is shown in Fig. 1a and at rates above 24/s in Fig. 1b (note the difference in scaling). At low shear rates, a viscosity increase is not noticed until a temperature of around 76 °C. The viscosity shows somewhat more complex behaviour at high shear rates. In Fig. 1b, a small viscosity increase is already noted around 40 °C, indicating aggregation phenomena. In agreement, the opaque tendency of the WPI suspensions increases at this temperature. Around 50 °C, the viscosity shows a small decrease, and finally a steady increase is observed at 70 °C, which is attributed to the denaturation of whey protein (Hegg, 1980). It may also be seen in Fig. 1 that the increase in viscosity is weaker

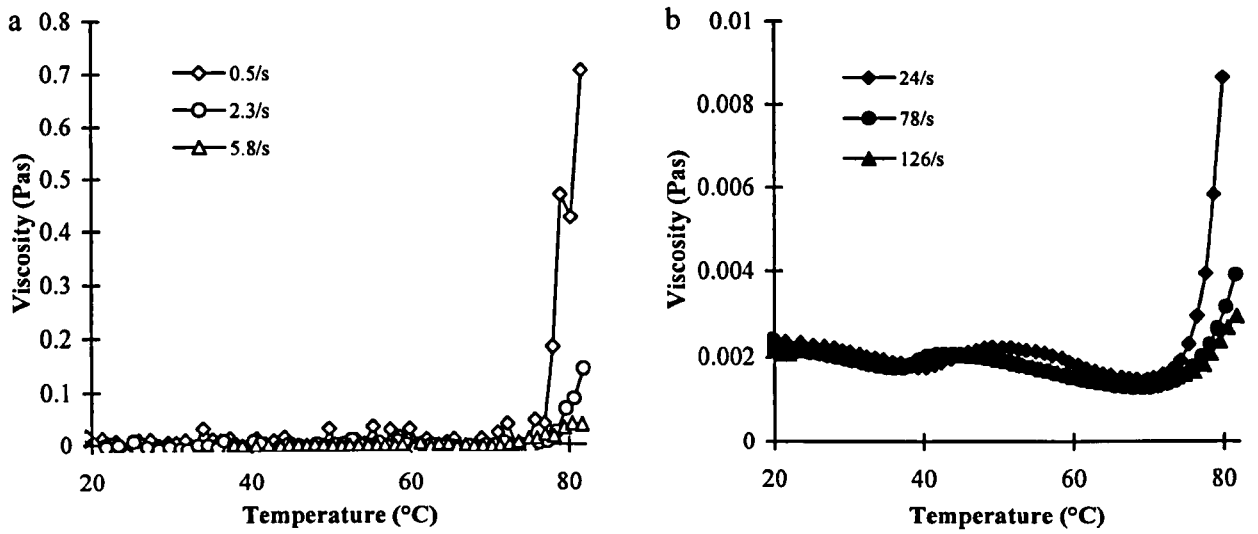

Fig. 1. Viscosity versus temperature increase from 20 to 82 °C, at various shear rates, for 10% w/w WPI suspensions at pH 5.4. (a) Shear rates less than 6/s; (b) shear rates above 24/s.

with an increase in shear rate. This behaviour is explained by aggregate break-up increasing with shear rate.

The different viscosity behaviour at the high and low shear rates can be a result of an increased number of particle collisions with an increased shear rate (Walstra & Jenness, 1984) (see Introduction regarding meeting frequency of particles, J_g). This stimulates the aggregation and leads to the earlier viscosity increase found in Fig. 1b. At temperatures around 40 °C, it is also possible that the sensitivity of the rheometer to detect any small changes in the viscosity is too low at the low shear rates.

Viscosity changes in whey protein suspensions at pH 7 during a temperature increase have been studied by Tang, Munro, & McCarthy (1993). At a constant shear rate of 291/s, a steady increase in viscosity started at a temperature of 60 °C. This result was interpreted in terms of structure formation in the suspensions. The viscosity behaviour found in this study under shear flow (Fig. 1) differs from that found by Tang et al. (1993). An explanation for the differences in flow behaviour is the pH-dependent aggregation behaviour of the whey proteins. The whey proteins are more prone to aggregate in the vicinity of the i.p. than above or below it. The complexity of the flow behaviour for whey protein suspensions at various concentrations and at pH-values between 6 and 10 has been demonstrated by Hermansson (1975). The experiments were performed at a fixed temperature of 25 °C and between shear rates of 0.01 and 1142/s. The whey protein suspensions showed various types of flow behaviour. Newtonian flow was found in the concentration range 4–12%. As the concentration increased up to 18–20%, the flow became pseudoplastic, and above 20% yield values were observed. As the pH increased, the viscosity parameters increased.

3.2. Microstructure of unsheared gels

A section of the unsheared gel is shown in Fig. 2 at two different magnifications. At the lower magnification (Fig. 2a), a homogeneous WPI network structure is revealed, composed of pores of even size, in the range of 50 μm, and particulate network strands. At the higher magnification in Fig. 2b, the aggregated network structure is shown in more detail. The unsheared network was mainly studied for comparison with the networks having a shear history. For more thorough investigations of network structure and rheological behaviour of pure whey protein gels formed under static conditions, see Langton & Hermansson (1992, 1996) and Walkenström & Hermansson (1994, 1998). Worth mentioning is that the WPI samples studied contain a small addition of NaCl, i.e. 0.05 M. It has been shown that the presence of salt increases the aggregation phenomena of

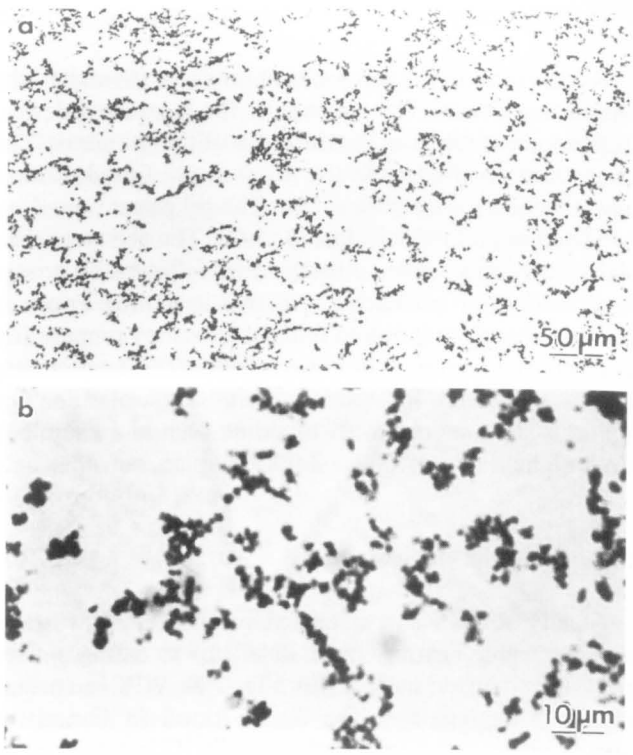

Fig. 2. Sections of an unsheared 10% w/w WPI gel at pH 5.4. (a) Low magnification; (b) high magnification.

whey proteins and results in more inhomogeneous network structures (Hermansson, 1979; Langton & Hermansson, 1996). The effects of the added NaCl on the WPI gels in this study have been investigated and proved to be minor, because the added NaCl concentration is low in relation to the mineral content of the WPI powder (see Material and Methods).

3.3. Effects on gels of steady shear below the gel point

3.3.1. Effects on microstructure

The effects on the microstructure of gels formed from suspensions exposed to low-rate steady shear (below 6/s) up to $T < T_g$, are shown in Fig. 3. The networks are homogeneous and similar, composed of pores of even size, around 50 μm, and strand-like aggregates. A small increase in inhomogeneity is suggested with an increase in shear rate, i.e. the gel having a shear rate history of 5.8/s seems to be more inhomogeneous, composed of larger pores and denser network areas. A comparison of the shear-treated gels in Fig. 3 and the unsheared gel in Fig. 2a shows that the shearing performed has less influence on the microstructure at this magnification. In a previous paper, the effects of short periods of steady shear in the vicinity of the gel point were investigated in whey protein gels (Walkenström & Hermansson, 1998). From a visual point of view, the networks with a shear history were similar to the unsheared network. However,

when image analysis was used to quantify the pore sizes, the shear-treated networks proved to be more inhomogeneous, being composed of different classes of pores (Walkenström & Hermansson, 1998). Thus, more studies are required to confirm any structural similarities or differences between the network structures in Figs. 2 and 3.

The dramatic effects on the microstructure of high shear rates, i.e. above 24/s, are evident from Fig. 4. The networks are irregular and coarse and very different in appearance to the unsheared network (Fig. 2a). Two different types of structures are present in the shear-treated gels in Fig. 4. One is open and loose. The other is extremely dense and compact, and seems to exist as individual, irregular aggregates. The different types of structure are shown in more detail in Fig. 5. The open, loose structure shows pores and particles of similar dimensions to those of the unsheared structure in Fig. 2. In contrast, the dense structure is composed of smaller particles and pores. Furthermore, an increase in the clustering phenomenon can be observed in the dense structure, i.e. several particles are fused together forming compact aggregates. In the unsheared network, the particles are linked more like a string of beads. It may also be seen in Fig. 4 that the dense aggregates decrease in size with shear rate. This behaviour is explained by increased shear forces with an increased shear rate, causing aggregate break-up. In agreement, a decrease in whey protein aggregate size with shear rate has been reported by Steventon et al. (1994). The behaviour was attributed to aggregate break-up mechanisms.

In suspensions exposed to high-rate steady shear, small aggregates can already be detected with the naked eye at a temperature around 50 °C. In relation to the size of the dense aggregates in Fig. 4, it is possible that these are the ones visually observed. It is suggested that

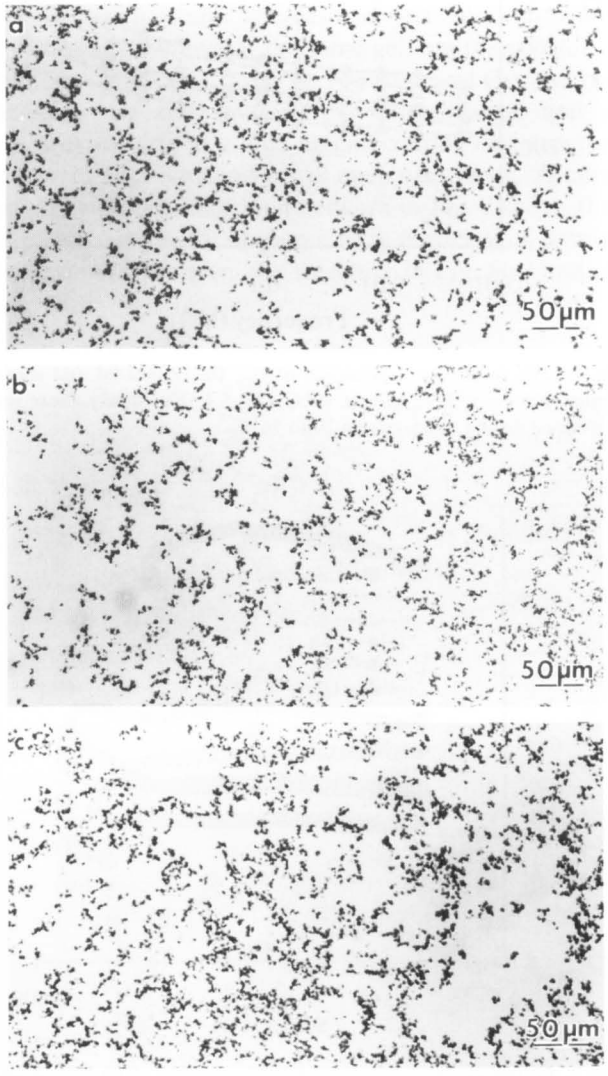

Fig. 3. Sections of 10% w/w WPI gels at pH 5.4 with a shear history of low rates during heating from 20 to 76 °C. (a) 0.5/s; (b) 2.3/s and (c) 5.8/s.

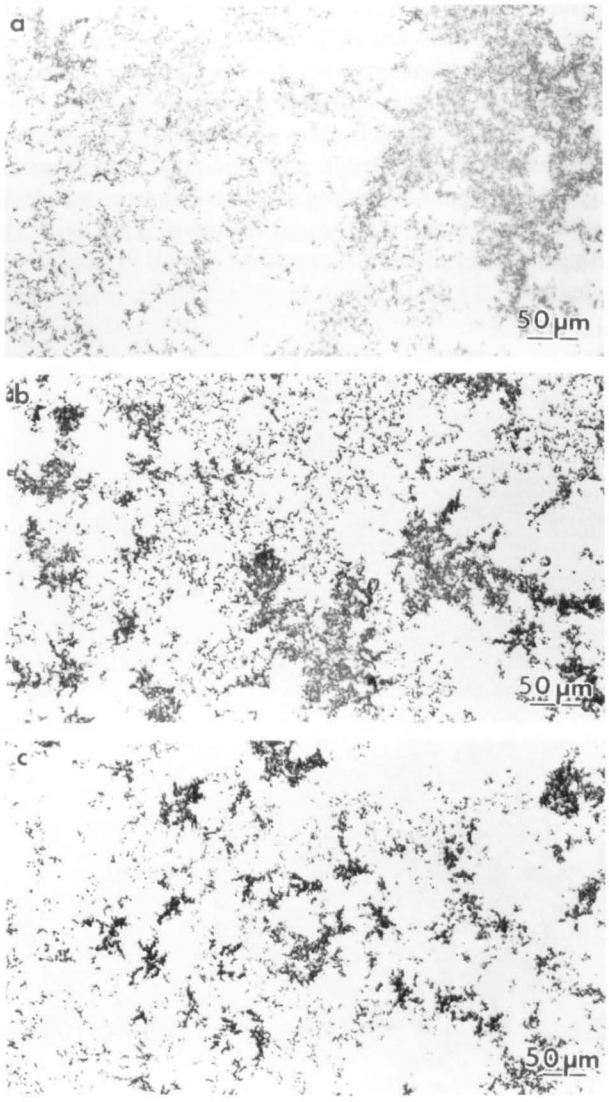

Fig. 4. Sections of 10% w/w WPI gels at pH 5.4 with a shear history of high rates during heating from 20 to 76 °C. (a) 24/s; (b) 78/s and (c) 126/s.

the dense aggregates (Fig. 4), with their small particles (Fig. 5b), are dynamic structures formed during the steady shear around 50 °C. In agreement with this suggestion, an aggregation phenomenon was indicated around 40 °C in the viscosity behaviour in Fig. 1b. The fact that the dense aggregates were absent in the shear-treated gels during the low rates (see Fig. 3) suggests that they are a result of an increased frequency of particle collisions with an increase in shear rate.

3.3.2. *Effects on rheological properties*

Fig. 6 shows the frequency dependence of the G′ for unsheared and shear-treated gels. The standard deviation, calculated from three to four measurements, is shown as error bars for some representative curves. Error bars have not been included on all curves to avoid cluttering of the graphs, but the variation is similar. The unsheared gel shows a higher G′ and frequency dependence than the shear-treated gels. For the rates considered, the G′ and frequency dependence of the shear-treated gels are more or less independent of the rate during the pre-shear up to a temperature below T_g. Thus, despite their totally different microstructure (Figs. 3 and 4), the gels show similar G′-values. A possible reason can be that the fine and open structure in Fig. 4 is the one responding to the oscillatory strain. As this structure is like that found for the gels in Fig. 3, the G′-values are similar.

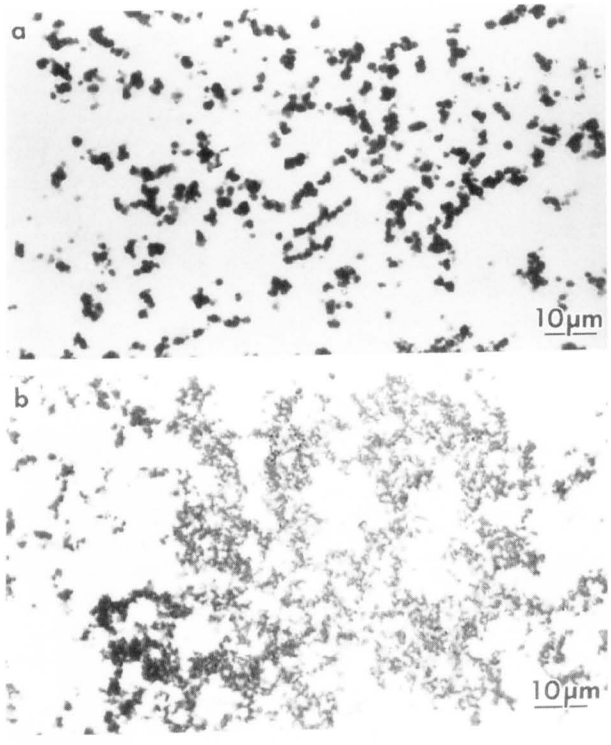

Fig. 5. Sections of a 10% w/w WPI gel at pH 5.4 with a shear history of 24/s during heating from 20 to 76 °C. (a) Loose network region and; (b) dense network region.

The stress sweep for the shear-treated gels up to $T < T_g$ is depicted in Fig. 7. In a dynamic stress sweep, the gels are submitted to a range of increasing stresses until they fracture. As can be seen in Fig. 7, the unsheared gel fracture at a lower stress than the shear-treated gels. The G′ of the unsheared gel starts to decrease at a stress of approximately 40 Pa and the fracture point takes place at around 150 Pa. The G′ of the shear-treated gels at rates less than 6/s already starts to decrease at a stress

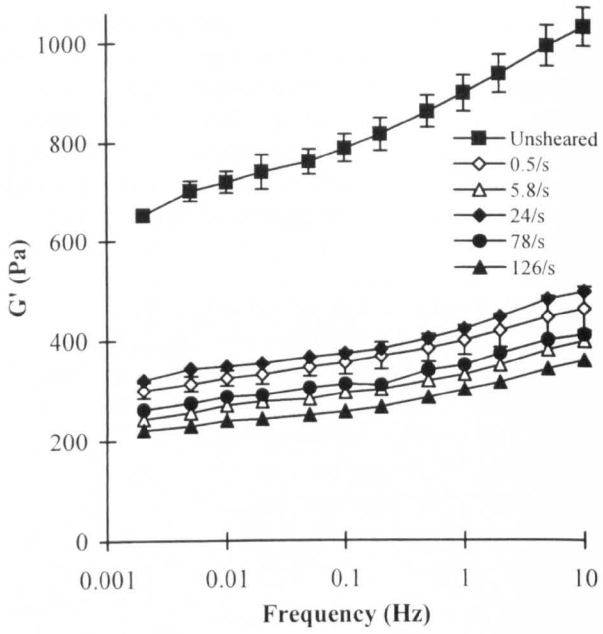

Fig. 6. The frequency dependence of $G'_{(f)}$ for unsheared and shear-treated 10% w/w WPI gels at 90 °C, pH 5.4. The steady shear was performed during heating from 20 to 76 °C.

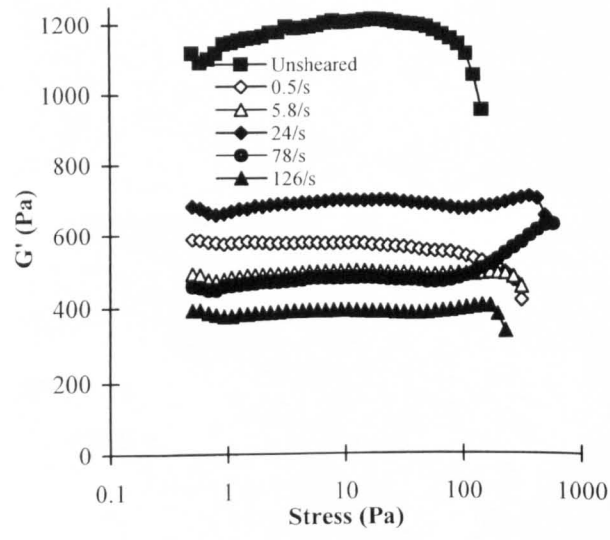

Fig. 7. G′ versus stress in a dynamic stress sweep of unsheared and shear-treated 10% w/w WPI gels at 90 °C, pH 5.4. The steady shear was performed during heating from 20 to 76 °C.

of approximately 20 Pa, but fracture does not take place until around 300 Pa. Thus, the linear viscoelastic region is narrower for the shear-treated gels than for the unsheared gel.

The gel shear-treated at 78/s shows a high stress at fracture ~550 Pa and a pronounced increase in the G′ before the fracture point. A similar but less pronounced increase in the G′ is found for the 24 and 126/s-treated gels. The increase in G′ before the break indicates a non-linear stress-strain relationship with an increasing apparent modulus on increasing strain. The results indicate that different types of structure found in the gels (see Fig. 4) have different mechanical properties and respond to the stress at various levels.

3.4. *Steady shear above the gel point*

3.4.1. *Effects on microstructure*

Gels with a shear history up to $T > T_g$, under shear rates less than ~6/s, are composed of two different types of network structure. The network structures shown in Fig. 8, originating from the same gel, are representative of those shear conditions. In Fig. 8(a) and (b), the two networks are shown at a low magnification and in Fig. 8(c) and (d), at a high magnification. The structure shown in Fig. 8(a) and (c) is open and loose. A comparison with the unsheared network in Fig. 2 shows that they are composed of pores and particles of similar dimensions. However, the structure in Fig. 8(a) and (c) is somewhat more inhomogeneous, showing denser network areas and some larger pores. The structure revealed in Fig. 8(b) and (d) is extremely dense and shows pores and particles of totally different dimensions than the unsheared network (Fig. 2). The large pores in the dense network are in the range of 10 μm (Fig. 8d), while in the unsheared network, they are in the range of 50 μm (Fig. 2a). It is noteworthy that the dimensions of the particles and pores in the dense structure are similar to those of the shear-induced aggregates in Figs. 4 and 5.

The two structures can be distinguished by visual observation of the gels and also by cutting them. The dense structure has a compact appearance and cutting with a scalpel shows it to have a stiff consistency. The open structure has a porous appearance. It is loose and soft, and is easily compressed when cut.

The fact that the dense network structure was absent in the gels shear-treated up to $T < T_g$ at rates less than ~6/s indicates that it is formed during the steady shear between 76 and 82 °C and is influenced by the denaturation of the WPI. The similarity with the shear-induced aggregates, formed under the high shear rates up to $T < T_g$ (see Figs. 4 and 5), suggests that the dense structure is induced by shear. A delicate balance between the shear-induced aggregate formation and break-up mechanisms determines the size of the dense structure domains.

The effects on the microstructure of a gel exposed to steady shear up to $T > T_g$ at a rate of 24/s is revealed in

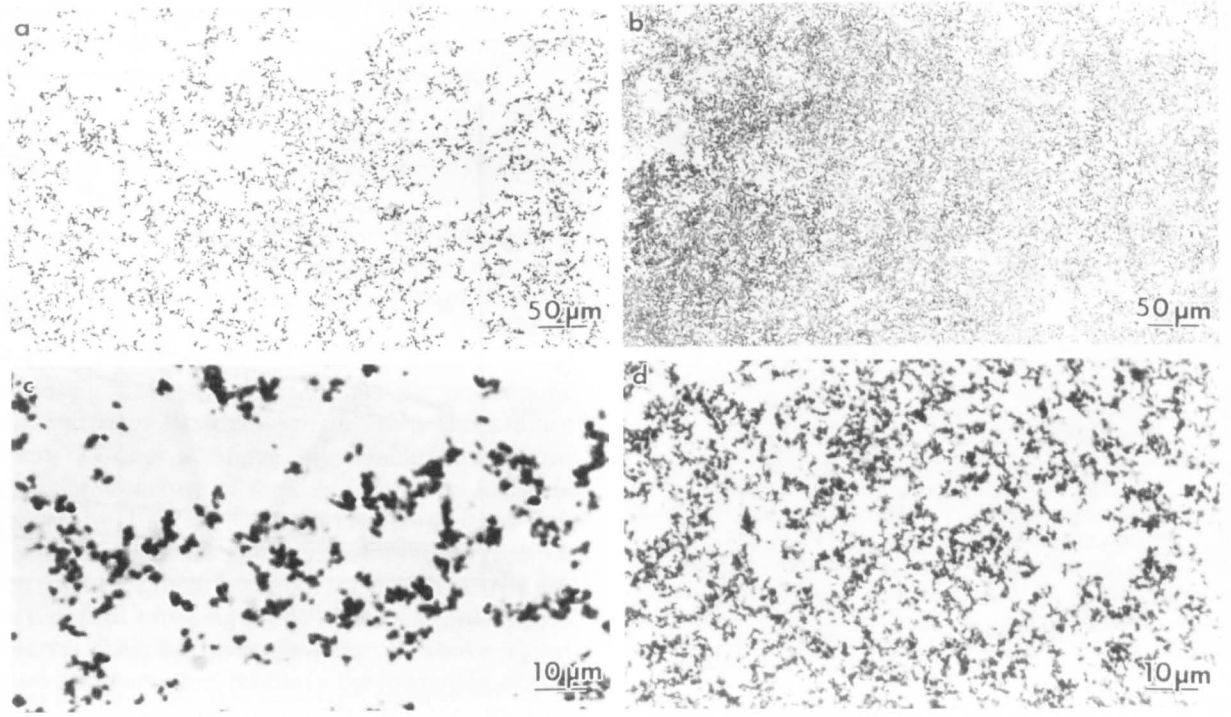

Fig. 8. Sections of a 10% w/w WPI gel at pH 5.4 with a shear history of 2.3/s during heating from 20 to 82 °C. (a) and (c) Loose network region; (b) and (d) dense network region.

Fig. 9. The network structure is coarse in appearance and inhomogeneous, composed of compact network areas and different classes of pores. The large pores are in the range of 100–200 μm, while the smaller are in the range of 10 μm. A comparison with effects found in the microstructure of shearing up to 76 °C reveals a similarity in the dimensions of particles and pores between the compact network areas in Fig. 9 and the suggested shear-induced aggregates (Figs. 4 and 5).

3.4.2. *Effects on the rheological properties*

The effects on the frequency dependence of G′ of gels with a history of various shear rates up to $T > T_g$ are shown in Fig. 10. A lower G′ and less frequency dependence are observed for the shear-treated gels than for the unsheared gel. This behaviour was also found for gels having a shear history up to $T < T_g$ (see Fig. 6). However, for rates less than 6/s higher G′-values result from shearing up to $T > T_g$ compared to $T < T_g$, while for the higher rates lower G′-values result.

The gels with a shear history of rates less than 6/s show a similar G′ and frequency dependence in Fig. 10. As can be seen in the inset in Fig. 10 (G′ at 1 Hz versus shear rate-history), an increase in shear rate above 6/s gives a dramatic decrease in the G′, indicating the existence of a critical shear rate above which aggregation break-up mechanisms become significant. The weak G′ found for gels treated at the high rates suggests that aggregate break-up mechanisms have dominated during the shear up to a temperature above T_g. This is further supported by the microstructure (Fig. 9), which showed a coarse and inhomogeneous network.

It may also be noticed from Fig. 10 that the frequency dependence of the shear-treated gels decreases with an increase in shear rate. An explanation for this behaviour is that the various network structures found for the gels (Figs. 8 and 9) have different relaxation times and, thus, respond differently to the frequency sweep. The relation between frequency dependence and microstructure of β-lactoglobulin gels has been studied by Stading et al. (Stading & Hermansson, 1990; Stading, Langton, & Hermansson, 1992). It was concluded that the structure of the β-lactoglobulin network as well as its homogeneity had a decisive effect on the behaviour towards a frequency sweep.

Dynamic stress sweeps for the shear-treated gels up to $T > T_g$ are shown in Fig. 11. The shear-treated gels show weaker stress at fracture and a narrower linear viscoelastic region than the unsheared gel, independent of the shear rate. The gels having a shear history up to $T < T_g$ fractured at a higher stress than the unsheared gel, independent of the rate during the shear (see Fig. 7). For the gels shear-treated at low rates, the break point takes place under a broad stress interval in Fig. 11.

The effects of short periods of shear treatment in the vicinity of the gel point have been investigated in

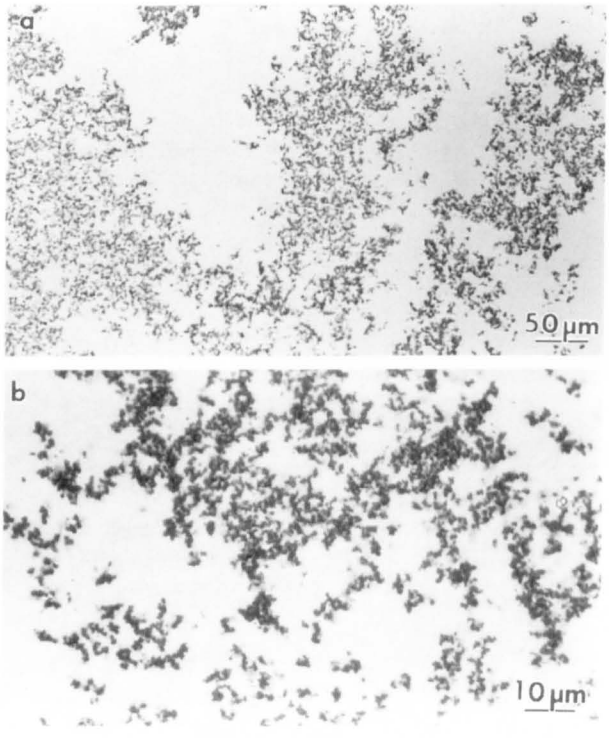

Fig. 9. Sections of a 10% w/w WPI gel at pH 5.4 with a shear history of 24/s during heating from 20 to 82 °C. (a) Low magnification; (b) high magnification.

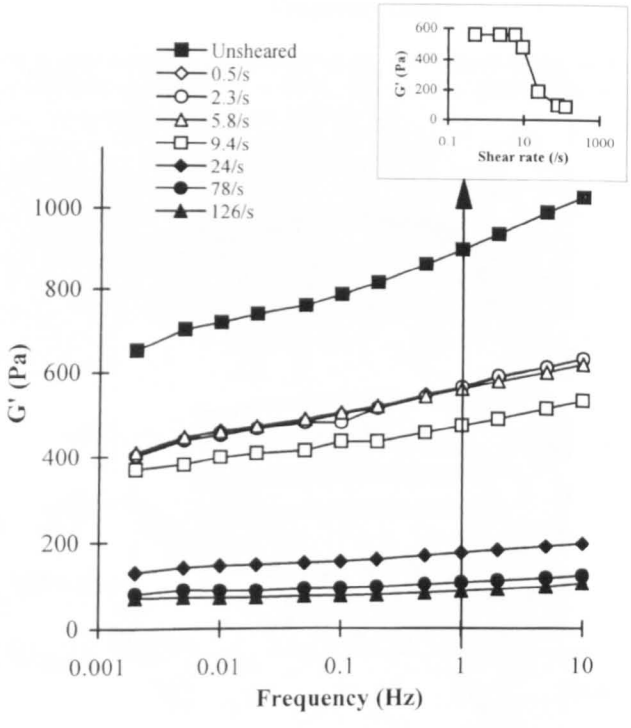

Fig. 10. The frequency dependence of $G'_{(f)}$ for unsheared and shear-treated 10%w/w WPI gels at 90 °C, pH 5.4. The steady shear was performed during heating from 20 to 82 °C. Inset: G′ at 1 Hz versus shear rate for the gels considered.

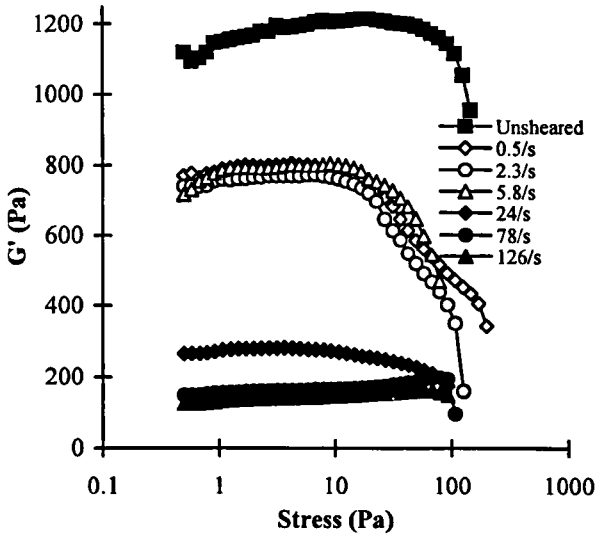

Fig. 11. G′ versus stress in a dynamic stress sweep of unsheared and shear-treated 10% w/w WPI gels at 90 °C, pH 5.4. The steady shear was performed during heating from 20 to 82 °C.

particulate whey protein suspensions by Walkenström & Hermansson (1998). The gels showed a G′ twice as high as that for the unsheared gel. There were no visible differences seen in light micrographs but, when quantifying the pore sizes by means of image analysis, it was found that the shear-treated gels were more inhomogeneous than the unsheared gels (Walkenström & Hermansson, 1998). In this paper, samples have been continuously sheared during heating from 20 to 76 or to 82 °C. These shear conditions have been shown to result in different rheological properties and microstructures. The differences are most likely caused by the various shear conditions in relation to the aggregation states of whey protein.

4. Conclusions

The network structure and the rheological properties of the WPI gels can be strongly influenced by exposing the suspensions to shear during a large part of the temperature induced aggregation.

- Exposing the WPI suspensions to continuous shear at rates less than ~6/s up to a temperature below T_g does not have any significant effect on the microstructure of the gels formed on the scale shown by LM. However, a lower G′, less frequency dependence and a higher stress at fracture are found for these gels than for the unsheared gel. In contrast, exposing the WPI suspensions to continuous shear up to a temperature above T_g, at rates less than ~6/s, results in the formation of two different types of network structure. One structure is open and loose, having similar particle and pore sizes to those in the unsheared network. The other structure is dense and compact, composed of smaller particles and pores. The latter gel also has a lower G′ and is less frequency-dependent than the unsheared gels, but in this case the stress at fracture is lower than for the unsheared gel.
- Networks having a steady rate history above 24/s, up to a temperature below T_g, are composed of different types of structure. An extremely dense and compact structure, present as individual, irregular aggregates, is interpreted to be a result of a shear-induced increase in the particle collision frequency. These networks show a weaker G′ and higher stress at fracture than the unsheared gel. Furthermore, a pronounced increase in G′ before the fracture point in a dynamic stress sweep is observed. During a steady shear at rates above 24/s up to a temperature above T_g, aggregate break-up is favoured, and the gels formed are composed of irregular and coarse networks. This gives a weak G′ as measured by dynamic oscillations.

Acknowledgements

The financial support from the Swedish Council for Forestry and Agricultural Research, SJFR, is gratefully acknowledged. Stephan Handschin is thanked for his support during the microstructural work. Mats Stading and Birgit Breitschuh are acknowledged for fruitful discussions during preparation of the paper.

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