

Aggregation of particle systems under shear

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ABSTRACT

The validity of a model for viscosity has been studied for an aggregating whey protein solution exposed to shear. The model has been found useful. As a part of the measurements, the effects of pre-shear at different shear rates on the storage modulus (G') of whey protein gels has also been investigated. When shearing at low rates, at a concentration of 14 % w/w, a higher G' -value was found compared to that for an unsheared gel.

INTRODUCTION

The aim was to determine the validity of a modelled viscosity of a solution of aggregated whey protein particles exposed to shear.

Under certain conditions, pH = 5.4, salt concentration 0.08 M and a temperature just below the gelation temperature, $T_g = 78$ °C, the whey protein shows a pronounced aggregation behaviour and forms spherical particles that flock to aggregates. This affects the viscosity and new models have to be worked out as the old ones do not include the changes in viscosity upon aggregation.

THEORY

In today's chemistry it is common to explain observable properties issued from intermolecular or intermacromolecular properties. For explaining the rheological

properties, e.g. viscosity, of a particle solution or gel, it becomes necessary to describe the geometry of the aggregates, the interactions between particles and the solvent, aggregates and the solvent, and the forces between the particles.

A model based on these properties for aggregating particles under shear have been presented by van Vliet and Kloek¹, based on work done by Sonntag and Russel² and Potanin and Uriev³. The modelling was done by modelling viscosity for non-aggregating particle suspensions, then adding a model for aggregation and, in the end, adding a model for aggregate break up due to shear.

If assuming:

1. The aggregates behave as non interacting spheres with a radius R and a fractal dimension D .
2. The aggregates are embedded in a homogeneous liquid with an effective viscosity η equal to that of the whole suspension.
3. On shearing, the shape of the aggregates does not change, but R decreases.
4. A mean field approach can be applied for the dependence of R on $\dot{\gamma}$.
5. The aggregates can be considered as being impermeable to liquid flow.

This results in:

$$\frac{\eta}{\eta_0} = \left[1 - \frac{\phi}{\phi_m^2} \left(\frac{2\sigma_m}{5\eta\dot{\gamma}} \right)^{m(3-D)} \right]^{-k_1\phi_m} \quad (1)$$

where η_0 was the viscosity of the solvent, ϕ the volume fraction particles, ϕ_m the maximum possible volume fraction, k_1 a factor of form, sphere, D the fractal dimension, m a factor of structure, σ_m the bond strength per particle cross section area between two primary particles and $\dot{\gamma}$ the shear rate.

EXPERIMENTAL

For the experiments a Whey Protein Isolate, WPI, was used, LACPRODAN® DI-9224, MD Food Ingredients, Videbaek, Denmark. The contents of the WPI was: 88% protein, less than 0.2% fat, less than 0.2% lactose, maximum 4% minerals and 6.08% moisture.

For sample preparation, WPI was mixed into a solution of distilled water and NaCl. The samples had a concentration of 6, 10 or 14 % w/w WPI. All samples had an equivalent salt concentration, including the minerals from the WPI, of 0.08 M NaCl. The solutions were mixed and degassed for 10 minutes. The pH-value was then adjusted with 0.5 M HCl to pH 5.40. Water was added to give the right concentration and the samples were degassed again for 10 minutes.

After preparation, a sample was directly poured into the measuring system of a Bohlin VOR Rheometer (Bohlin Rheology, Chichester, UK). A couette measuring system was used with a bob-diameter of 25 mm and a cup-diameter of 27.5 mm. The bob was surrounded by the WPI solution and a thin layer of paraffin oil was put on the top to prevent the sample from drying during the measurements.

Under a constant heating rate of 2.5 °C/min the samples were sheared from 20°C to 76°C with a steady shear-rate of either 0, 0.01, 0.46 or 46 s⁻¹. From 76°C to

90°C there was no shearing but instead a dynamic oscillatory measurement every second minute, with the frequency of 1 Hz and a strain of 1.5*10⁻³, in act to monitor the gel formation i.e. to obtain a G' vs. T curve. At a temperature of 90°C the sample was held for 60 min and then a frequency-sweep was executed. Then the temperature was decreased down to 20°C with a rate of -2.5°C/min and the temperature was hold for 60 min, with continued dynamic oscillatory measurements. At the end there was a second frequency-sweep followed by a strain-sweep.

RESULTS

Viscosity

The viscosity, η , was measured as apparent viscosity for the different shear rates during the heating from 20 °C to 76 °C. The viscosity at 74.5 °C is presented in Fig. 1. Due to the equipment it was not possible to optimise the measurements for both the viscosity below 76 °C and the G' at the end. The equipment was optimised for G' and therefore an unknown measurement error should be added to the statistic deviation. The values have small deviation except 6% w/w with shear rate 0.01 and 14 % w/w with shear rate 0.46. In Fig. 1 measured viscosities are compared with viscosities calculated according to the model for the concentration of 10 % w/w.

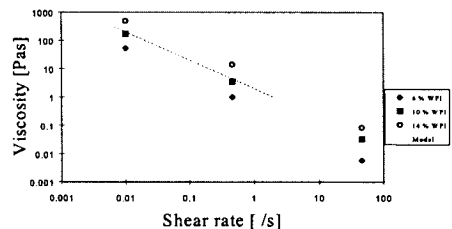


Figure 1. Modelled viscosity for 10 % w/w WPI compared to measured.

Storage modulus

The effect of a pre-shear of 0.46 s^{-1} on the G' of gels with different concentrations is seen in Fig. 2.

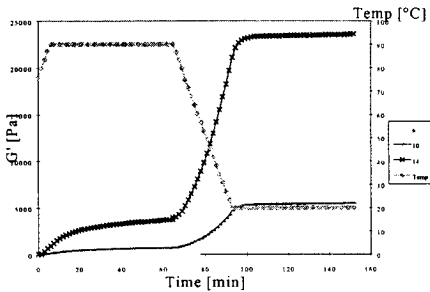


Figure 2. G' and Temperature vs. time for gels sheared by shear rate 0.46 s^{-1} with different WPI concentrations.

For the samples sheared with shear rate 0.46 s^{-1} there is a clear and expected relation between an increase in the concentration and an increase in the storage modulus for the gels. Time zero in Fig. 2 corresponds to the time when passing T_g . During the time for reaching equilibrium at 90 °C there is a small increase in G' , indicating that all particles have not aggregated around T_g . When the temperature drops from 90 °C down to 20 °C , there is a large and rapid increase in G' . At the low temperature plateau, 20 °C , there is also a small increase in G' corresponding to the one at 90 °C , but the slope is smaller, hence indicating that the value of G' at 20 °C is closer to the temperature dependent equilibrium value.

The same trends were found for gels exposed to shear rates of 0.01 s^{-1} and 46 s^{-1} , prior to gel formation. Furthermore, the unsheared sample also followed the same trends.

When comparing the effect of different shear rates on G' of gels with the same concentration, there were large difference between the investigated concentrations 6, 10 and 14 %w/w WPI.

For 6 % w/w WPI (Fig. 3), the unsheared sample had the highest average

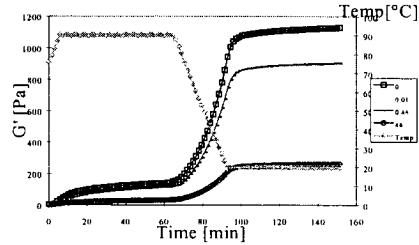


Figure 3. G' and Temperature vs. time for gels sheared by different shear rate with WPI concentrations of 6 % w/w.

G' and the sample sheared at 0.46 s^{-1} had the second highest. This reciprocal sequence was statistically significant except within unsheared and 0.46 s^{-1} .

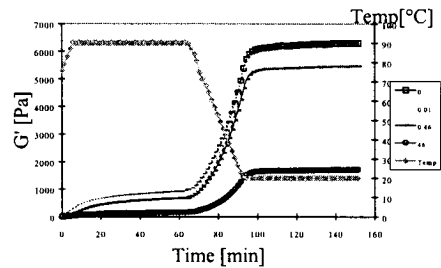


Figure 4. G' and Temperature vs. time for gels sheared by different shear rate with WPI concentrations of 10 % w/w.

For 10 % w/w WPI, a decreasing tendency for the average values was detected for an increasing shear rate (Fig. 4), but with large deviations present there was no statistically significant tendency. In fact the only statistically significant difference, was that the G' for the shear rate of 46 s^{-1} was lower than the other shear rates.

For 14 % w/w WPI, the measurements show a higher G' for both the shear rate of 0.46 s^{-1} and 0.01 s^{-1} than for the unsheared. The tendency here was that G' increases for

small values of shear rate and then G' drops to low values again at the highest shear rate.

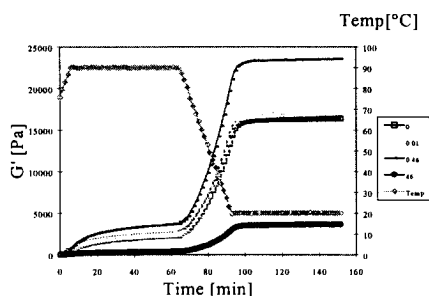


Figure 5. G' and Temperature vs. time for gels sheared by different shear rate with WPI concentrations of 14 % w/w.

DISCUSSION

The result of G' of WPI-gels exposed to different shear-rates, shows interesting and surprising results. When comparing G' with WPI concentration, ϕ , the trends were clear. In general, a concentration of 14 % w/w gave the highest G' followed by 10 % w/w and then with the lowest G' , came 6 % w/w, hence an increase in ϕ resulted in an increase in G' . With G' clearly depending on ϕ , one would expect a similar dependence on the volume fraction of aggregates, ϕ_a .

Shear could effect ϕ_a in the way that if an increase of shear rate makes the aggregates more compact and hence decreases the volume of the sphere. A decrease of volume must also decrease ϕ_a , and therefore decrease G' . If this is true the shape of the modelled η curve will be the same as the curve for G' . As shown in the figures above, this was only true for a WPI concentration of 10 % w/w when comparing different shear rates but not for 6 and 14 % w/w and hence another mechanism must also be present.

The trends are more clearly seen if a relative storage modulus is used.

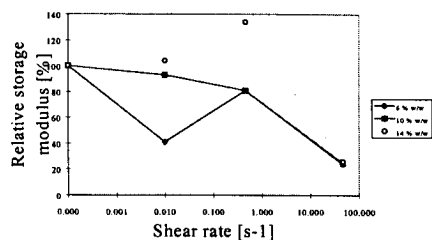


Figure 6. Relative storage modulus vs. shear rate.

The result for WPI concentration of 10 % w/w was in agreement with results by Walkenström and Hermansson⁴. Walkenström et.al.⁵ has also showed a shear induced increase in G' , as here shown for 14 % w/w, when shearing in the vicinity of the gel point for short times.

REFERENCES

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