Monitoring a Particle Aggregation Process

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ABSTRACT

Build-up of particle aggregates was followed by viscosity measurements and with direct observation by a sequence of micrographs, taken in an unstopped 3D flow field, with a confocal laser-scanning microscope. After aggregation had reached a steady state, a shear thinning behaviour was detected and analysed.

INTRODUCTION

The aggregation process of particle systems in general is of rheological interest for a wide area of fields, such as wastewater treatment, optical properties of ink, pulp pumping, mineral-recovery, nuclear material in power plants, blood coagulation and food production. The processes are often well suitable to be monitored for process-control by rheology-measurements. However, to enable an accurate micro-structural interpretation or to investigate different process steps, complementary techniques are often demanded.

In this investigation, the strategy was to monitor the aggregation process not only by viscosity measurements, but also to by direct observations with microscopy. The used model process was aggregation under shear of latex particles coated with whey protein, in a continuous phase with a complex rheological behaviour.

MATERIALS & METHODS

Monodisperse polystyrene latex particles, of 5μm, known as SOURCE 5RPC, were acquired from Amersham Pharmacia Biotech, Uppsala, Sweden. Whey protein isolate, (WPI) LACPRODAN® DI-9224, was obtained from MD Foods Ingredients Amba, Viby, Denmark. Gelatine was obtained from Extraco, Klippan, Sweden.

Preparation

The dispersion of whey coated polystyrene latex particles was prepared by dissolving the latex particles in a small volume of a water/ethanol. Sodium chloride, rhodamin, whey protein concentrate and water were added and the pH was then adjusted to 5.4 with small amounts of HCl.

Another solution containing 10 % gelatine, 10 % sucrose, sodium chloride was prepared in a small beaker. The solution was heated to 60 °C to dissolve the gelatine and reduce the amount of dissolved gases in the solution. The temperature was reduced to around 30°C.

As a final step, the particle dispersion was mixed with the same amount of gelatine solution. The dispersion was regulated and kept at 30°C for 10 min during stirring to avoid gel-formation of the gelatine.

Rheology

The viscosity measurements were made in a Bohlin VOR Rheometer (Bolin

Rehology, Chichester, UK) equiped with the Millennium software (Bholin Reologi, Öved, Sweden). The measuring system consisted of a cup and bob with double-gap geometry. The inner and outer walls (diameter 21.7 mm and 27.4 mm) rotated during measuring while the bob (diameter 23.9 mm to 24.9 mm) was fixed. During the measurements, the Taylor numbers were always in the region of 0.3 to 6 $*10^{-7}$; thus they were far below the critical number of 3 400 for Taylor vortices.

Direct observations

The used dispersions for the monitoring were prepared at the same way as for the rheology studies. After the preparation, the dispersion was poured into a Four-Roll Mill, 4-RM. The 4-RM generates a complex 2D-flow, ref.

The 4-RM was adjusted to fit under a Confocal Laser-Scanning Microscope.

Process

The process was a temperature profile together with a continuous flow. The temperature profile started at 30°C and rose to 60 °C in 900 s, with a slope of 2 °C min^{-1}. The temperature was then held at 60 °C for 4500 s. In the viscosity-measurements, the flow-type was exclusively shear. Three different shear rates were used 0.05 s^{-1}, 0.5 s^{-1} and 5 s^{-1}. In the direct observations, the flow was a mixture of shear and elongation with a stagnation point in the centre where the microscope was focused.

RESULTS

The result of the viscosity measurement at the three shear rates are shown in figure 1. The profiles can be divided into three different sections.
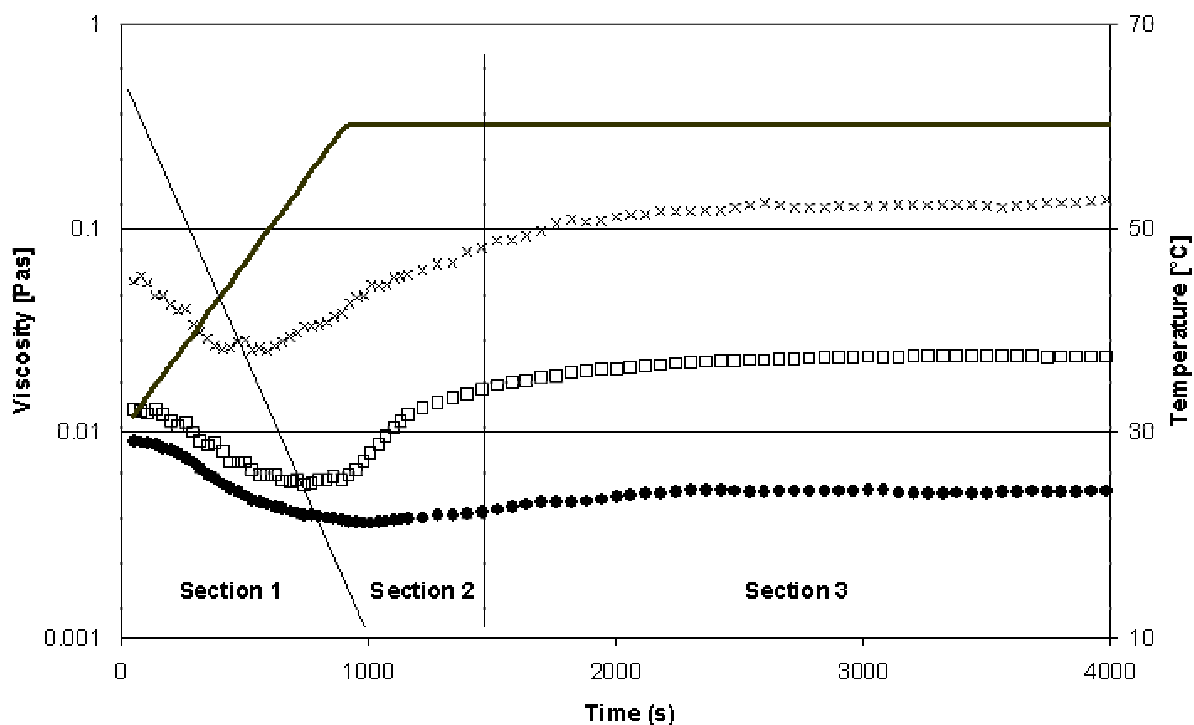

Figure 1. Build-up of particle aggregates followed by viscosity measurements for three shear-rates, × 0.05. □ 0.5, and ● 5.0 s^{-1}. Measured process temperature – °C
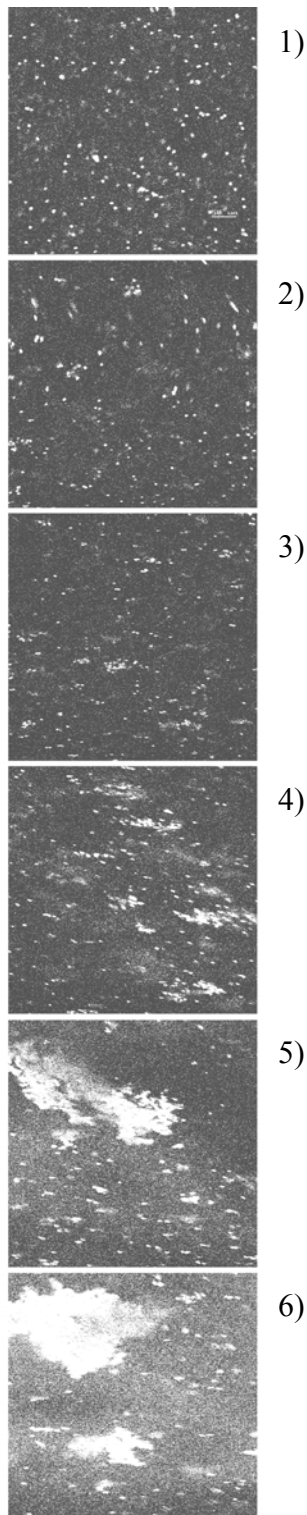
Figure 2. Build-up of particle aggregates followed by CLSM-micrographs. From [1]. Temperature and time: 1) 30 °C, 0 s; 2) 40 °C, 300 s; 3) 50 °C, 600 s; 4) 60 °C, 900 s; 5) 60 °C, 1200 s; 6) 60 °C, 2000 s.

Section 1: Temperature decrease and onset of aggregation

The decrease for all graphs in section 1 is due to the temperature-induced fall in viscosity in the continuous-phase when the temperature drops from 60 C to 30 C in the 900 first seconds. However, the decrease for the three shear-rates are not equal and differs in there time required for the decrease. The decrease in viscosity due to temperature should not be shear-dependent and therefore this difference in viscosity decrease is explained by the onset of aggregation. At the low temperatures at early stages, the incipient aggregation results in fragile aggregates that could be disrupted as the shear decreases the overall aggregate growth by introducing break-up and rearrangements.

Section 2: Aggregation

The steep rise of the viscosity, in section 2, occurs mainly after the dispersion has reached 60 °C. The increase in viscosity is due to an accelerated aggregation of the whey-coated particles. When the temperature has reached 60 °C, the forces that hold the particles together seem to be strong enough to let the aggregates overcome the break-up and to grow.

Section 3: Steady state

In the final region of the viscosity profile measurements presented in figure 1, the viscosity has reached steady state values. The steady state viscosity values are 130 ± 27 mPas for 0.05 s^{-1}, 23.1 ± 2.7 mPas for 0.5 s^{-1} and 5.16 ± 0.40 mPas for 5 s^{-1}.

Direct observation

The actual development of the aggregation could also bee seen in the micrograph-sequence in figure 2. The first micrograph is from the start when the temperature is 30°C. The particles are present as singles in the thick continuous phase.

59

The second micrograph was taken after 300 s at a temperature of 40°C. The particles are still singlet, but the viscosity is decreasing. In the third micrograph a small aggregation is visible as some of the particles have started to aggregate into doublets. The temperature of the solution is 50°C, time is 600 s, and the overall viscosity is near its minimum.

The next micrograph was taken at 900 s and at the temperature of 60°C. The viscosity is increasing rapidly as the aggregates grow. At 1200 s, in the fifth micrograph the temperature is held at 60°C. Large aggregates are present and the viscosity is near its steady state. In the final micrograph, after 2000 s, both the aggregates and the viscosity have reached its final state. The temperature is 60°C.

Shear thinning

To analyse the phenomena underlying the shear-thinning behaviour of the dispersion at the steady state, additional viscosity measurement were done directly after 5 000 s. The additional viscosity measurements were also performed at the shear rates of 0.05 s^{-1}, 0.5 s^{-1} and 5 s^{-1}; and the results are presented in the end of figure 3. The viscosity for all dispersions showed to be decreasing for higher measuring-shear-rates. However, the values were also highly dependent on what shear-rate they were subjected to during the aggregation, pre-shear-rate.

Comparing the viscosities within the group with the same measuring shear rate reveals a viscosity difference that is due to structural changes in the dispersion. If the viscosities with the same pre-shear rates were compared instead, this would reveal the differences due to shear thinning. Hence, the conclusion is that the clear difference in viscosity value for the differing shear rates is due to two separate effects: the shear thinning in the continuous phase and the structural changes of the aggregates. The mutual relationship during
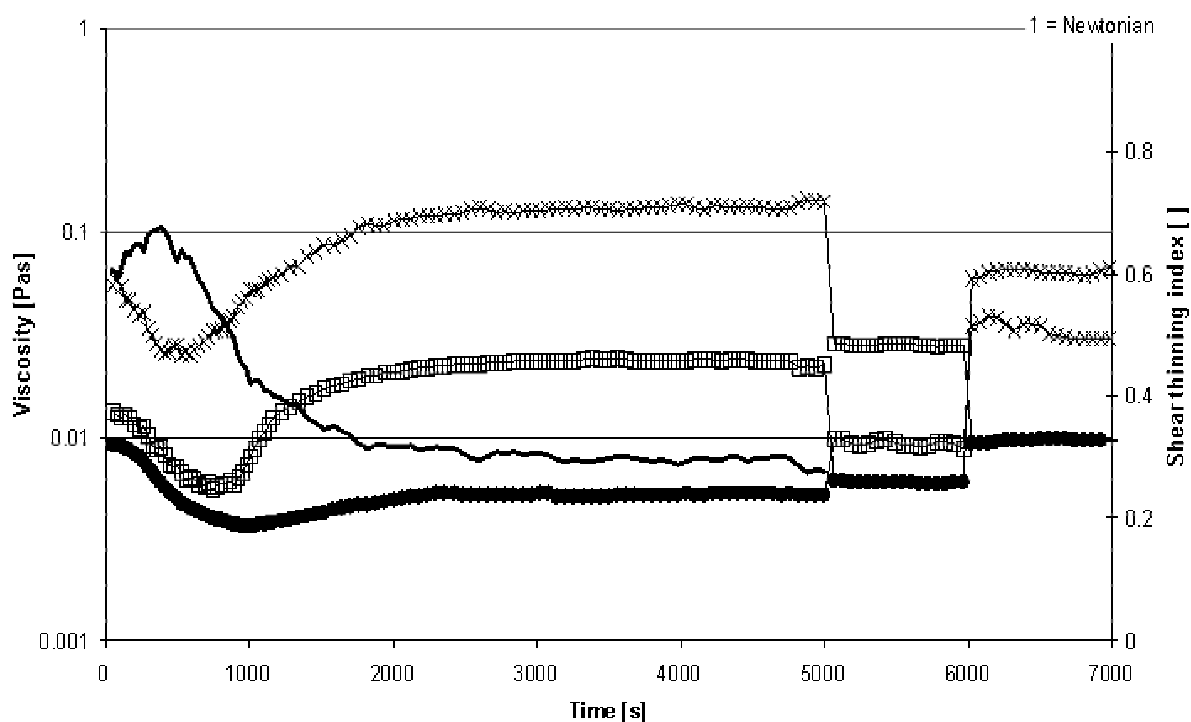

Figure 3. Viscosity at different shear- rates, after 5000 s, × 0.05. □ 0.5, and ● 5.0 s^{-1}, connected to the different pre-shear measurements, before 5000 s. The solid line, − before 5000 s represents the shear-thinning-index, n.

the pre-shear for viscosity, η, between the curves with different shear rates, γ is well described by a power law relationship such as:

$$\eta = m\gamma^{(n-1)}. \qquad (1)$$

The value of n is the shear thinning index $n = 1$ for a Newtonian fluid with no shear thinning. The coefficient m, normally depends on temperature and concentration (Macosko,1994). Extracting the index n as a function of time from the curves in figure 3 gives an initial value of n at around 0.6. The shear thinning index, n, develops further with time at around 500 s it reaches its maximum of 0.7, after which the value starts to decrease. After 1500 s, n is stable at around 0.3 and the value remains the same until the end of the measurements. This means that the increase in shear thinning behaviour of the dispersion does not start until the temperature has reached approximately 45°C.

Based on the shapes of the curve and together with the micrographs in figure 2, the conclusion is that: the shear-thinning index seams to monitor the aggregation better than the actual viscosity curves.

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