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Visualization of the breakdown of dilute particles gels during steady-shear

Abstract A feature of models concerning the rheology of coagulated suspensions is the development of shear planes. An experimental setup was developed in which we investigated, by visual analysis, whether shear planes really develop in such systems during steady-shear. A transparent coagulated PTFE dispersion was used, in which the refractive indices of the continuous and dispersed phases were matched, for the formation of a gel. Coagulation was effected by adding NaCl to a concentration of 0.5 M. Polystyrene particles were built into the gel structure as tracer particles. During steady-shear the velocities and trajectories of the tracer particles were analyzed by Particle Tracking Velocimetry (PTV). Indeed layers with approximately the same velocity were observed for a coagulated PTFE-gel, during steady-shear. Deviations from rectilinear motion of the tracer particles were observed. These observations correspond with the assumptions of the giant floc model in which the shear is not distributed homogeneously, but limited to certain shear planes. Deviations from rectilinear motion of the tracer particles in a dilute gel correspond with the results found by Folkersma et al. (1998) in which the distance by which a moving particle entrains its neighbours was assumed to be larger at low volume fractions (≈0.1) than at high volume fractions (≈0.4).

Key words Gels – steady-shear – PTV – tracer particles

Introduction

The rheological properties of gel-like or aggregating systems are widely studied. However, the structural changes that occur when these kinds of gels are subjected to steady-shear flow, are still not understood. Verduin et al. (1996) investigated the structural changes of a colloidal gel subjected to a steady-shear flow. The model dispersion of these authors consisted of stearyl coated silica spheres dispersed in benzene. They found, by using small-angle light scattering, at small shear rates, formation of regularly spaced large structures in the flow direction; when the shear rate was increased, the structures were disrupted to smaller units. Melrose and Heyes (1993) also studied the rheology of weakly flocculated suspensions by simulation of agglomerates under shear. They concluded that at low shear rate the agglomerates are deformable bodies, at higher shear rates the agglomerates become unstable and the system undergoes a morphological transformation to layers parallel to the shear axis.

The giant floc model (Van Diemen and Stein, 1983, 1984; Schreuder and Stein, 1987; Laven et al., 1988) is based on the same idea (see section on Theory). The model starts from the idea that, at low shear rates, the shear is not distributed homogeneously but limited to certain shear planes. In the present paper the development of an experimental set-up is reported in which we investigated by visual analysis whether those shear planes really develop during steady-shear.
We used a transparent PTFE dispersion (solid volume fraction ≈ 0.17), in which the refractive indices of the continuous and dispersed phases were matched (Kops-Werkhoven et al., 1981, 1982; Piazza et al., 1990; Mannheimer, 1990). Polystyrene particles (volume fraction: $\phi \approx 5 \cdot 10^{-5}$) were built into the gel structure as tracer particles. Coagulation was induced by electrolyte addition.

During steady-shear the velocities and trajectories of the tracer particles were analyzed by Particle Tracking Velocimetry (PTV). The use of tracer particles in sheared and turbulent transparent dispersions has been reported by Graham and Bird (1984) and Komasawa et al. (1974). Graham concluded from his visual analysis that clusters are continuously created and destroyed during shear and that these clusters translate and rotate.

In this paper, an investigation is reported on the question of whether it is possible to prepare transparent particle gels containing tracer particles, and whether it was optically possible to follow such small tracer particles ($d = 3 \mu m$) in a shear flow. In addition, we investigated whether on deformation of such gels shear planes could be observed.

**Theory**

The giant floc model (Van Diemen and Stein, 1983, 1984; Schreuder et al., 1986, 1987; Laven et al., 1988)

The giant floc model has been developed for coagulated suspensions of high solid volume fraction (larger than about 0.35) in which separation of discrete flocs is not observed even if densities are not matched. Use of the overall solid volume fraction for characterizing the local environment of a particle then introduces a negligible error. When such a “giant floc” is subjected to a shearing stress, the shear will not develop homogeneously at low stresses, but in preferential shear planes, only at relatively “weak spots” in the gel. In the model, these shear planes are idealised as flat planes parallel to the direction of motion, with an average separation of $A$. It may be questioned whether the existence of shear planes in the direction of motion is a reasonable assumption.

A shear plane separates two domains in which a given particle remains surrounded essentially by the same neighbours. We assume that the continuous phase moves with the mean velocity of the flocs. Particles in the border of a domain are found in the shear planes. On the average, they each occupy an area $A^2$ in this plane.

When shear occurs in a shear plane, a particle bordering this plane meets particles from the adjacent domain. In the direction of motion, two such particles approaching each other are separated on the average by a distance $A\cdot \cos u$ (where $u$ is the angle between the direction of motion and the line connecting the centers of the two particles).

When such a collision is imminent, the particles involved are forced out of their way over a certain distance $\delta_0$. Because of hydrodynamic interaction the particles do not really collide in most cases; nevertheless the process is here named a “collision”. In the model, the distance $\delta_0$ is more important than whether or not a real collision occurs. Thus the present model is insensitive towards the value of the capture efficiency (Van de Ven, 1989).

A colliding particle is bound to $q-1$ neighbours in its own domain, where $q$ is the average number of neighbours of a particle within a domain. The colliding particles drag these neighbours each over an average distance $\delta_0 t$ (with $0<\delta<1$). These neighbours in turn drag their $q-1$ other neighbours over a distance $\delta_0 t^2$ etc.

The energy dissipated by a particle moving over a distance $\delta$ in time $t$ is given by:

$$\varepsilon_p = \text{force} \cdot \text{distance} = 6 \pi \eta_0 af \cdot \delta/t \cdot \delta$$  \hspace{1cm} (1)

where $a$ is the particle radius, $\eta_0$ the viscosity of the dispersing medium, and $f$ the frictional ratio (= quotient between actual friction and friction as calculated for an isolated sphere). Thus, one collision is accompanied by an energy dissipation:

$$\varepsilon_c = 2 \cdot 6 \pi \eta_0 af \left[ \frac{\delta^2}{t_0} + (q - 1) \frac{t^2}{t_1^2} \frac{\delta^2}{t_0} + \ldots \right]$$

$$= 12 \pi \eta_0 af \frac{\delta^2}{t_0} \frac{1}{1 - (q - 1)^2}$$  \hspace{1cm} (2)

Here use is made of the fact that the time during which the particles move is equal to $t_0$ for all particles dragged during one collision.

The energy dissipated per unit volume and time is then obtained by multiplying $\varepsilon_c$ by the number of particles in shear planes per unit volume ($=2/(A^2)$) divided by 2, because we counted two particles in adjacent planes in Eq. (1), and divided by the time between two successive collisions ($A \cdot \cos u/\langle \gamma A \rangle$). In addition, $t_0 = \delta_0 / (\gamma A \cos u)$. We obtain:

$$\dot{\varepsilon} = 12 \pi \eta_0 af \frac{\delta_0 A}{A} \frac{f}{A^2} \frac{1}{1 - (q - 1)^2} \gamma^2$$  \hspace{1cm} (3)

This would correspond with Newtonian behaviour if all parameters (except $\dot{\varepsilon}$) were independent of $\gamma$. However, especially $A$ is expected to decrease with increasing shear rate and shear stress: a region able to withstand a small shear stress may break down on application of a larger one. Thus, at low $\gamma$ values not all potential shear planes are operational.
PTV (Particle Tracking Velocimetry)

PTV is characterized by the following properties (Van der Plas and Jansen, 1996):

1) it permits tracking of trajectories of individual particles in a 2D flow field in 2D space,
2) it allows the determination of two components of particle velocities inside an observation space in a moving fluid,
3) the particles are assumed to follow the motion of the small fluid elements in which they are embedded, so limitations are imposed on the size and mass density of the particles. This is only important when the velocity of the fluid must be measured.

In particle tracking, a gel is provided with tracer particles (in our case polystyrene). The tracer particles are homogeneously distributed in the coherent network of the particle gel. Polystyrene tracer particles were chosen because it is important that the tracer particles are small and their density is close to that of the continuous phase (water). In such a case the tracer particles will move with almost the same velocity as the fluid does locally. Tracking the tracer particles will therefore give information about the local fluid velocity.

Projection of a laser sheet (1×2 mm) through the transparent gel will visualize the movement of the tracer particles in a two-dimensional slice of the gel. By using a video-camera, images of the illuminated tracer particles are recorded on video-tape. The particle path information is determined by automated analysis of the recorded video-images.

The analysis proceeds as follows: with equally spaced time intervals, video images (also called frames) are taken from video-tape and the positions of the tracer particles are located in each frame. In order to determine the particle paths between two images indicated as 1 and 2, resp., we need a way to figure out which particle image in frame 1 corresponds with which particle image in frame 2 (all images of particles are indistinguishable from each other). This is done by means of a matching algorithm, which determines the most likely combinations between the particle images in image 1 and image 2. The likelihood or probability of a particle image combination is given by a so-called cost function.

For matching, one has to define a cost function to express the likelihood that one particle image in one frame and another particle image in the next frame corresponds to the same physical particle in the flow field. A solver using the cost function is then applied to find the best set of pairings between two images. It is reasonable to require the average inter-frame displacement of particles to be smaller than the mean minimum distance between particles. In that case the following basic evaluation function can be used:

\[ c_{ij}^f = \| x_{ij}^{f+1} - x_{ij}^f \| \]  

where \( x_{ij}^f \) is the estimated position of particle \( j \) from frame \( f-1 \) in frame \( f \). Low values of \( c_{ij}^f \) correspond with a high probability that two images are a pair. More detailed information concerning the mathematics in particle tracking has been published by Bourgeois and Lalanne (1971). For the analysis of our data we used Dig-Image as developed by Dalziel (1993).

Experimental

Materials

The experiments were performed with a FEP dispersion (FEP=tetrafluoroethylene-perfluoropropylene, Du Pont de Nemours). FEP is a copolymer of PTFE (polytetrafluoroethylene); it is a negatively charged, hydrophobic colloid containing FEP resin particles suspended in water by a non-ionic wetting agent as stabilizer. The particle size as specified by the manufacturer is 0.1–0.25 μm. The particles are not perfectly spherical, but rather have an ellipsoid-like shape. After dispersion of these particles in pure water, a suspension is formed which was coagulated by adding NaCl up to a final concentration of 0.5 M. Thus we are dealing, in aqueous PTFE dispersions, with a gel in which the cohesion between the particles is due to coagulation. In a dummy experiment, the cell was filled with a dispersion of polystyrene in water, in the absence of electrolyte, showing no signs of coagulation. In this latter case we are dealing with a non-coagulated dispersion, i.e. not with a gel.

Rheological measurements

The rheometer used for the viscosity experiments was a Carri-Med Weissenberg Rheogoniometer (TA Instruments Ltd.) equipped with a static cone-ended cylindrical bob in a concentrically rotating cylindrical bob with flat bottom (Mooney-Ewart). (For the specifications see Folkersma et al., 1998.)

A FEP-gel was used at a volume fraction of 0.17 and contained polystyrene tracer particles with a volume fraction of 5·10⁻⁵; the shear rate applied was 0.2 s⁻¹.

Matching the refractive index of the FEP-dispersions

Refractive indexes of the FEP-particles and the continuous phase were matched by adding sucrose (ex. Janssen Chimica, p.a.). Refractive indices were measured with a
PTV

The video images were analyzed using the DigImage package. DigImage is a MS-DOS-based image processing system, specially developed for Fluid Dynamics by Stuart Dalziel at the Department of Applied Mathematics and Theoretical Physics of Cambridge University (Dalziel, 1993). The software holds, beside a PTV function, a number of standard functions for image processing, e.g. functions for filtering, contouring, image enhancement, etc. The experimental set-up is illustrated in Fig. 1. A is the rotating (transparent) cup, B is a stationary disk (Teflon), C is a laser diode (iLee 28/LDA2011, wavelength 680 nm), D are mirrors placed at 45° to direct the laser sheet through the gap of the Couette geometry and in the microscope (E), F is a video camera connected with a video recording system (G). The video images were analyzed afterwards using the DigImage set-up (H), particle tracking was applied on a video recording (standard: PAL-SVHS) of 5 minutes, I is the torsion measuring assembly of the rheometer.

Results and discussion

Rheological measurements

Steady-shear rheological curves are plotted in Fig. 2, showing the quotient $\eta/\eta_0$ as a function of shear rate. $\eta$ is the viscosity, $\eta_0$ is the viscosity of the liquid medium. The measurements were performed for the following volume fractions: 0.023, 0.054, 0.081, 0.097 and 0.12. At high volume fractions ($\phi \geq 0.097$), measurements at low shear rates ($<10 \text{ s}^{-1}$) turned out to be unreliable due to wall slip. At low volume fractions ($\phi \leq 0.054$) the sample in the gap cannot be considered macroscopically homogeneous any more, resulting in instability of the measurements.
Sedimentation becomes significant on the time scale of the experiment (at $\phi \leq 0.054$), since the aggregate radii are rather large at these volume fractions, and the density of the FEP particles is rather high ($2.0 \times 10^3 \text{ kg/m}^3$).

In this paper we describe the visualization of the breakdown of dilute particle gels during steady shear; we are dealing with a percolated network. The experimental evidence that we are dealing with, with a gel, at $\phi > 0.054$, arises from:

i) in Fig. 2 the slope of the curves at low shear rates is approximately equal to $-1$,

ii) no separate flocs could be observed,

iii) tracer particles were fixed in the network; there were no movements of separate tracer particles on small deformations (oscillations) of the gel, but were movements of the tracer particles in phase.

The conclusion is justified that gels are formed and that they show a shear thinning behaviour.

**Refractive index matching**

Figure 3 shows a plot of the specific turbidity as a function of the index of refraction of the dispersion. In order to keep the volume fraction of particles constant, a correction was applied at high sucrose concentrations. The turbidity never goes to zero, that is, it is impossible to optically match particles and continuous phase completely. The minimum turbidity corresponds to a weight fraction of sucrose of 14.6%. The fact that the index of refraction cannot be matched totally indicates that a PTFE particle has a complicated internal structure which includes both amorphous and crystalline regions, making the FEP particles optically inhomogeneous.

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**Fig. 3** Specific turbidity as a function of the refractive index of the dispersion

**Fig. 4** Four images, at different time steps of the velocity vectors of polystyrene spheres in water. Shown is one-fifth of the gap width. Bottom of the images corresponds to the stationary disk. Shear rate applied is 0.2 s$^{-1}$. 
PTV

In Fig. 4, four images of the velocity vectors at different time steps are shown for a non-coagulating polystyrene dispersion. The velocity vectors presented are in the \(x/y\)-plane (the plane of the laser sheet).

In Fig. 5, four images of the velocity vectors at different time steps are shown for a FEP gel. The velocity vectors presented are in the \(x/y\)-plane (the plane of the laser sheet).

Figure 6 compares the velocity as a function of the position in the gap for the non-coagulated polystyrene/water system and for the coagulated FEP-gel.

Figure 6 shows that in the case of the coagulated dispersion the velocity distribution does not show a smooth proportionality of the distance from the wall in the case of the FEP-gel; on the contrary, layers are observed in which the tracer particles have about the same velocity. In the absence of a coagulated gel (i.e. in the PS/water system), the solid particles have a velocity which increase linearly in the arrangement shown (Fig. 1), however the velocity gradient starts not at the origin of Fig. 6. This may be due to the difficulty of maintaining strictly laminar conditions near the stationary disk, because of flows around the edges of the stationary disk which disturb the velocities of the tracer particles.

In the presence of a coagulated gel, the increase of the velocity with increasing distance from the wall is much less regular. Especially at distances between 30 and 95 \(\mu\)m, and between 120 and 150 \(\mu\)m from the wall, regions with approximately equal tracer velocities can be discerned. These observations correspond with the assumptions of the giant floc model: the shear is not distributed homogeneously but is primarily limited to certain shear planes (Folkesma et al., 1998). Indeed, the conclusion is justified that different layers in the gel
can be observed, because we have analyzed 60 images and the average values (also considering the errors) show that the differences between the two lines in Fig. 6 are still significant.

As can be seen from Fig. 5 the velocity of the tracer particles in the FEP-gel is not always directed in the horizontal direction ($x$-direction). Figure 7 shows the component of the velocity vectors in the $y$-direction as a function of the position in the gap. According to the giant floc model, the fraction of distance by which a moving particle entrains its neighbours is equal to $l$. In (Folkersma et al. 1998) it is concluded that the experimental flow curves for dilute gels could be fitted well, using the giant floc model, when the parameter $l$ was increased, compared to a concentrated gel system. This conclusion seems justified because in a concentrated system there is no space for the particles to deviate from rectilinear motion during a collision (particles obstruct each other). In a dilute system, however, there is, and that can also be concluded from Fig. 7, in which some particles move in the $y$-direction. Especially loose parts of the domains may show a rotation.

**Conclusions**

Layers with approximately the same velocity were observed for a FEP-gel, during steady-shear. These observations correspond with the assumptions of the giant floc model in which the shear is not distributed homogeneously but is principally limited to certain shear planes. Also, deviations from rectilinear motion of the tracer particles were observed. Deviations from rectilinear motion of the tracer particles in a dilute gel correspond with the results found in Folkersma et al. (1998), in which an increase in $l$ (fraction of distance by which a moving particle entrains its neighbours) was assumed, at low volume fractions, to fit the experimental flow curves.

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**References**


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