STABILITY AND FLOW INDUCED AGGREGATION OF CONCENTRATED POLYMER DISPERSIONS

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1   Introduction

Stability of flowing suspensions of small particles is strongly affected by the kinematics of the bulk flow and by the forces acting between particles. There are many experimental and analytical studies of particle aggregation in simple shear flow. An analysis of a shear induced flocculation under conditions such that Brownian motion of the particles is unimportant, consists in determining particle trajectories, taking into account hydrodynamic interactions and nonhydrodynamic forces between the particles [1]. In many technical processes fluids are often exposed to complex flow fields including strong extensional components (diverging or converging stream lines). Theoretical findings show that colloidal particles aggregate much more easily in an extensional flow field than in pure shear flow, since the streamlines converge and hence the contact time between colliding particles increases. This phenomenon is called flow-induced aggregation [2]. It is relevant not only for classical technical operations like coating, pumping or filtration, but also for the application of concentrated suspension in upcoming processing technologies based on microfluidic devices.

Despite its importance the aggregation process in extentional flow fields is still not well understood. An investigation of the process of clogging microchannels using poly-(dimethylsiloxane) microfluidic devices concentrate on the understanding of the blockage mechanism at the level of a single pore [3]. It shows that the formation of clogs is determined solely by a critical number of particles that flow through the single pores and stick irreversibly to the sidewall at constriction, when their distance of approach is comparable to the length scale of the attractive surface forces. This work provides an insight into the dynamics of clogging in a pore network on the single pore level but it is restricted to very dilute suspensions.

Our study focus on the aggregation process of concentrated polymer dispersions exposed to extensional flow-field. In order to investigate this phenomenon experimentally a ring-slit device has been developed capturing the essential features of a strongly converging flow field [4]. This

device embodies a capillary viscometer and a ring-slit die. The ring-slit geometry allows us to maintain a small gap height and a large cross-sectional area at the same time, corresponding to a high contraction ratio. When aggregation takes place the slit entrance is gradually clogged resulting in a strong pressure increase. Thus this technique enables us to study the stability of colloidal suspensions in converging flow-fields and offer the advantage of simultaneously formation and "detection" of the aggregates.

Our experiments aim at getting a better understanding of the mechanisms that lead to flow-induced aggregation. The dynamics of the aggregation process are to be investigated in terms of the dependence on the flow kinematics, colloidal interaction forces, dispersion properties and the particle-wall interactions. In this work we report experimental results that show the influence of the volumetric flow rate and the slit height, as flow kinematics parameters and the effect of the colloid volume fraction on the aggregation probability in strongly converging flow field.

We also check the effect of particle deformability on the aggregation phenomenon of soft and hard polymer particles.

2 Experimental

2.1 Materials

The main material studied in this work is an adhesive formulation for the shoe industry. It is supplied by Bayer MaterialScience AG as a raw material. This system is a polyurethane dispersion synthesized by the acetone process [5]. The polyurethane ionomers are formulated in an organic polar solution and spontaneously form dispersions when water is stirred in. As the water added gradually the hydrophobic chain segments of the polymer become insoluble and kind of microprecipitation results from the initial aggregation. Owing to the stabilizing effect of the ionic groups, tiny globules will form which contain a core of aggregated soft segments and a boundary layer carrying the ionic groups. The final step is the removal of the organic solvent by distillation.

The investigated commercial polyurethane dispersion is an elecrostatically stabilized anionic dispersion. The system stabilization arises from the formation of electrical double layer between the ionised sulfonate surface groups and the monovalent counterions. The average particle size is about 116 nm and the breadth of the particle size distribution is estimated at $\pm$ 10% of the average size. The as-received raw dispersion is at pH of 7 and has a solids concentration of 43% by weight. The viscosity at room temperature is relatively low, in the range of 50-600 mPas. The glass transition temperature of the polymer is – 40°C.

Polystyrene dispersion is used to compare its flow stability as a hard polymer dispersion with the stability of the dispersion of soft polyurethane particles exposed to the converging flow field. The investigated polystyrene dispersion is a commercial product available from Dow Chemical Company. It is also highly concentrated dispersion with solids concentration of 48% by weight. The dispersion is received at pH of 5.5 and average particle size 140 nm. The polystyrene particles have glass transition temperature far above the T_g of the polyurethane, namely 95°C. The characteristics of the investigated samples are summarized in *Table 1*.

Table 1: Properties of the investigated dispersions.

Property	Polystyrene dispersion	Polyurethane dispersion
Solids content / wt.%	48	43
Glass transition temperature / °C	95	- 40
Particle diameter / nm	140	116
pH	5.5	7

2.2   Experimental Apparatus and Procedure

Schematic diagram of the experimental apparatus is shown in *figure 1a*. It consists of a capillary viscometer and a ring-slit die mounted to the bottom end of the wall of a cylindrical sample reservoir. The sample is forced to flow through the ring-shaped slit with a constant volumetric flow rate, which is controlled by setting the piston speed. A pressure transducer mounted above the die records the corresponding extrusion pressure as a function of time or extruded sample volume. If the sample is stable the pressure adjusts itself to a comparably low constant value determined by the viscosity of the particular sample (*fig. 1b*). In this case the instrument operates as a high shear capillary rheometer and apparent shear rates, apparent shear stresses and correspondingly the viscosity can be calculated according to:

$$\dot{\gamma}_{app} = \frac{6\dot{V}}{B \cdot H^2}$$

with $\dot{V} = \pi \cdot R^2 \cdot v$, $\tau_{app} = \dfrac{p \cdot H}{2L}$ and $\eta_{app} = \dfrac{\tau_{app}}{\dot{\gamma}_{app}}$

If the sample is not stable, the formatted aggregates in the converging flow field at the entrance of the slit clog the slit cross-section and the extrusion pressure increase with the time.

The slit height can be varied between 10 and 50 µm which is more than 50 times larger than the particle size of the investigated samples. The angle at the slit entrance and the length of the en-

trance region is correspondingly 45° and 1mm. The technical specifications of our experimental set-up are summarized in *table 2*.

Table 2: Technical specifications of the ring-slit device

Specification	Value
Radius **R** of cylindrical sample chamber	12 mm
Gap height **H**	10-30 µm
Mean gap width **B = 2πR**	62.8 mm
Gap length **L**	1 mm
Entrance length **L`**	1 mm
Entrance angle α	45°

All samples are pre-filtered through a 25 µm filter, in order to remove aggregates eventually formed in previous processing steps.

**(a) Ring-slit device**   **(b) Extruded volume vs. pressure**
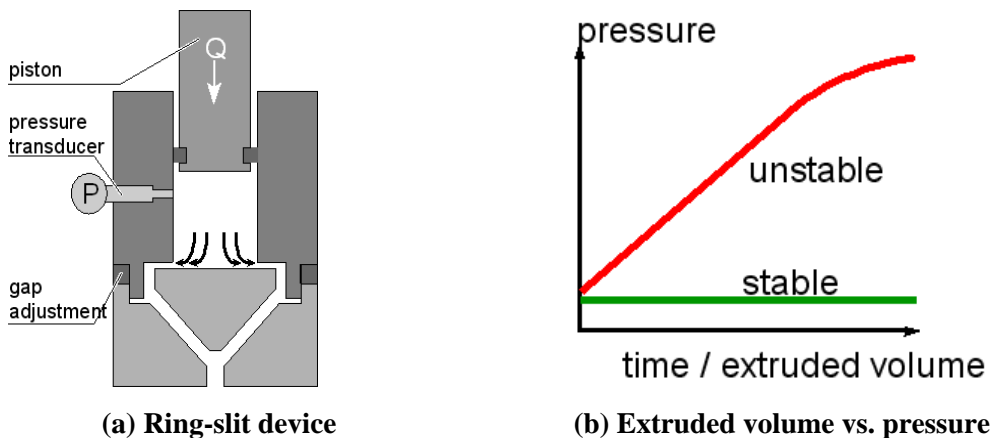
Fig. 1: Ring-slit device (a) and pressure development for stable and unstable samples (b)

In this study the samples are extruded repeatedly through the ring-slit with four different piston speeds, so that the flow rate is in the range between 63 mm³/s and 4710 mm³/s. Recorded pressure during each measurement is required to be normalised by so called viscous pressure, the initial pressure reading that correspond to the viscosity of the particular sample, in order to be able to compare the pressure increase due only to the aggregate formation at different flow rates, slit heights, different solids content or other parameters that influence the viscosity and respectively the corresponding pressure drop.

3 Results and Discussion

3.1 Flow Kinematics

Systematic study of the aggregation probability of flowing suspensions requires variation of flow and material properties. CFD simulations show that elongational flow is pre-dominant in the entrance region of the ring-slit, hence volumetric flow rate and slit height as well as the length and the angle of the entrance region have to be varied to investigate this aspect of flow-induced aggregation. The effect of the flow rate on the stability of the commercial polyurethane dispersion has been investigated by repeating the experiment at four different piston speeds. For this data we fix the slit height to 10 μm. The results presented in f*igure 2* show strong flow rate dependence. A great pressure increase is observed when the sample is extruded at the lowest piston speed. Obviously, in this case fast aggregation takes place and the flow stability becomes better with increasing the flow rate. We explain these results with decreasing the contact time between colliding particles with increasing flow rate and consequently decreased aggregation probability in the converging flow field at the entrance of the slit.
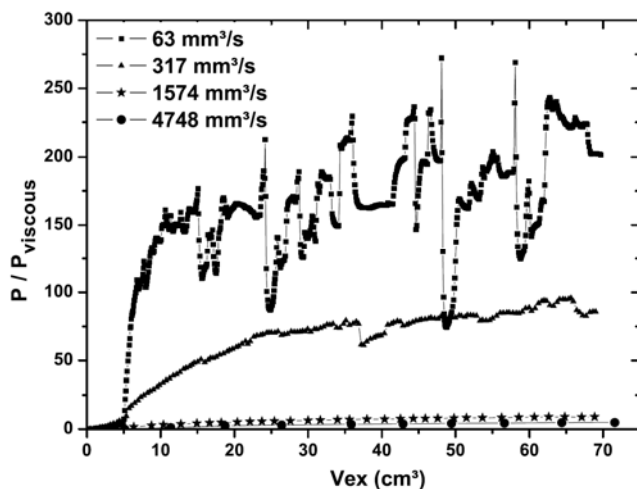
Fig. 2: Effect of flow rate on the stability of the commercial polyurethane dispersion (s.c. 43%; gap h = 10 μm)

The influence of the slit height on the flow induced aggregation at a constant flow rate is shown in *figure 3a*. As the gap height varies from 10 μm to 30 μm the dispersion stability varies from unstable with high pressure increase to completely stable. When we compare the flow stability of the same sample extruded at equal shear rate with the three different slit heights we still observe the same slit height dependence but combined with the effect of the flow rate, which is increased with increasing the slit height in order to keep the shear rate constant. The results are presented in *figure 3b*.
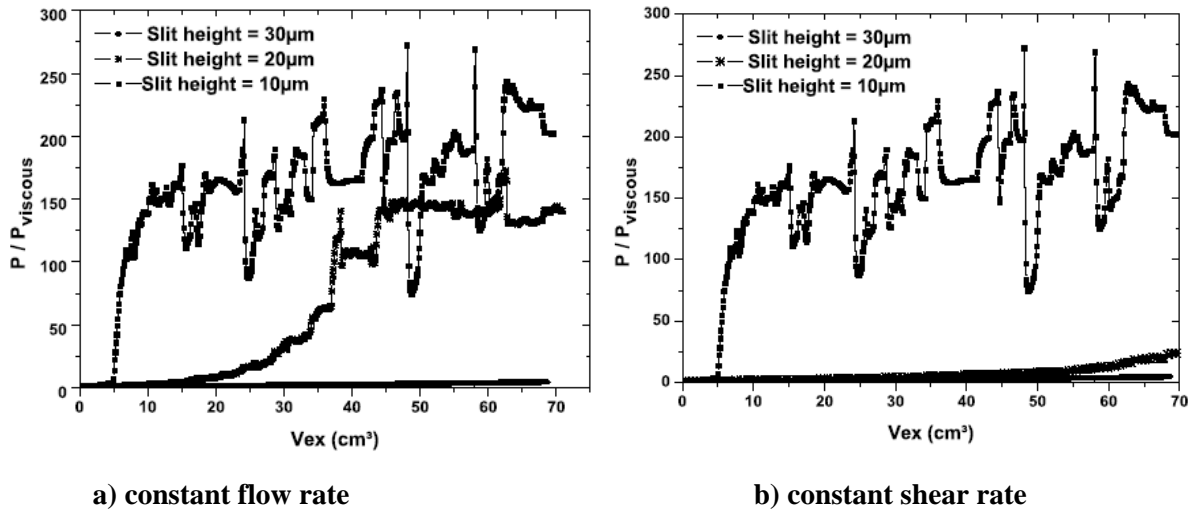
a) constant flow rate   b) constant shear rate

Fig. 3: Effect of slit height on the stability of the commercial polyurethane dispersion with s.c. 43% compared at constant flow rate = 63 mm³/s (a); compared at constant shear rate = 59713 s⁻¹(b)

This data is an indication that the deformation rate is not a relevant parameter responsible for the aggregation probability but rather deformation which can be characterised by the total contraction factor at the slit entrance defined by the ratio H/R. It is also required to investigate the influence of the entrance angle to further elucidate this effect.
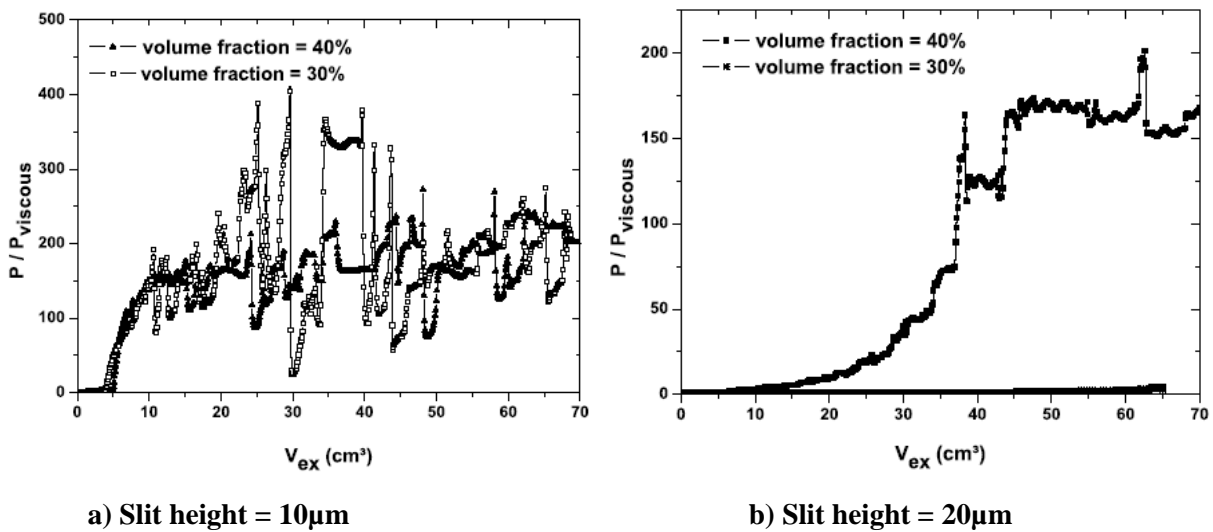

a) Slit height = 10µm   b) Slit height = 20µm

Fig. 4: Effect of volume fraction on the stability of the commercial polyurethane dispersion (flow rate = 63 mm³/s) at slit height 10 µm (a) and slit height 20µm (b)

Further contribution to this hypothesis based on the correlation between the total contraction factor at the slit entrance and the mean particle separation are the results of investigation the effect of particle concentration. The commercial polyurethane dispersion is diluted from 40% to 30% volume fraction and extruded through the 10µm and 20µm slit, while keeping all the other parameters constant. As shown in *figure 4a* and *figure 4b* decreasing the concentration of the polyurethane dispersion its flow stability does not change by extrusion through the 10µm slit but

in the case of the 20µm slit height the concentration effect is well pronounced and the sample can be considered stable in the case of 30% volume fraction. Therefore we suppose a critical volume fraction under which the mean particle separation is so large that the total deformation is not high enough to bring the particles sufficiently close. Further experiments are necessary to determine the volume fraction threshold for the 10µm and 30µm slit. We are working on it.

3.2   Particle properties

Besides flow kinematics the properties of the suspended particles them selves are supposed to have a strong effect on the aggregation. The suspensions investigated here are stabilized by repulsive interactions and are designed for a shelf-life of more than six months. The polyurethane dispersion is stabilized by surface charges due to ionised sulfonate groups. The interaction potential is determined by the charge density on the particle surface and the ionic strength in the surrounding liquid. We estimate the range of the interaction potential by mapping the divergence in the zero-shear viscosity onto that on hard spheres [1]. The zero-shear viscosities are extracted from well-defined Newtonian low-shear plateaus observed for volume fractions up to 37%, shown in *figure 5*. As a result the range of electrostatic repulsion, based on the effective excluded volume is determined to be 8 nm. A consequent study of the effect of ionic strength on dispersion stability is going to be performed, dialysing the polyurethane sample against salt solutions of various concentrations.
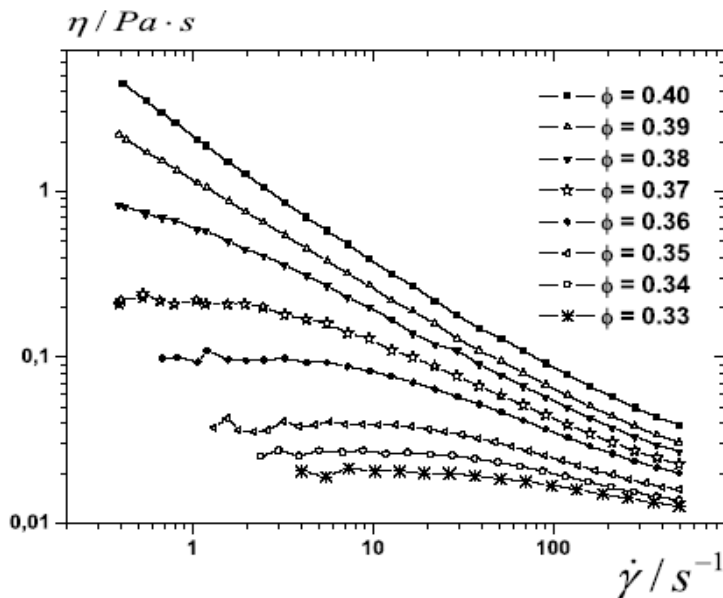
Fig. 5: Shear viscosity as a function of shear rate for the commercial polyurethane dispersion

Another characteristic feature of the investigated polyurethane dispersion is the low glass transition temperature, accordingly we assume that the forces accompanying the extrusion are suffi-

cient to compress and deform the particles, at least at the highest flow rate. In contrast to the polyurethane dispersion, the polystyrene is a high T_g polymer and the hard polymer particles do not deform during extrusion. In order to compare the flow stability of dispersions with soft and hard polymer particles with similar particle size, volume fraction and stabilization mechanism we tested the aqueous polystyrene dispersion in the ring-slit device, the results are shown in *figure 6*. Moderate increase of the pressure signal is observed when the sample is extruded at low flow rate and a constant pressure signal is detected at higher flow rate. The polystyrene dispersion shows similar behaviour in the ring-slit test as the polyurethane dispersion.
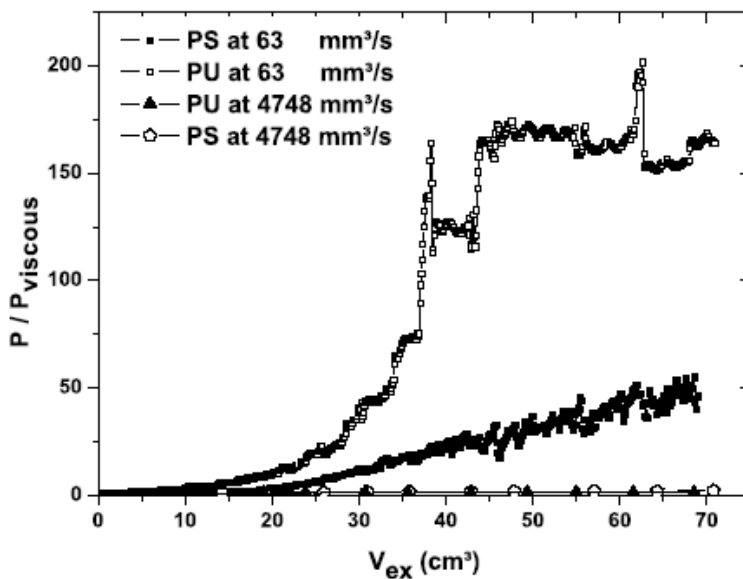
Fig. 6: Effect of flow rate on the stability of the polystyrene dispersion (PS) and the polyurethane dispersion (PU); gap h=20 µm

3.3   Conclusion

Our ring-slit device captures the dependence of aggregation probability on relevant experimental parameters, thus providing a general picture for the dynamics of aggregation process under elongational flow conditions. We have shown that the volumetric flow rate and the slit height variation strongly influence the aggregation probability of the investigated highly concentrated suspensions exposed to the extensional flow field at the entrance of the ring-slit. The results of the flow rate influence on the flow induced aggregation are explained in term of the contact time between colliding particles which decrease increasing the flow rate. The slit height variation results in a data which imply that the deformation rate is not a relevant parameter responsible for the aggregation probability but rather deformation which can be characterised by the total contraction factor at the slit entrance. We are going to extend this investigation of the flow kinematics parameters varying the length and the angle of the entrance region.

Since the investigated polyurethane dispersion is highly concentrated, electrostatically stabilized dispersions one needs to account for the effect of solid content and ionic strength on dispersion stability. The results of investigation the effect of particle concentration in the case of different slit heights suggest a critical volume fraction under which the mean particle separation is so large that the total deformation is not high enough to bring the particles sufficiently close. We have also estimated the range of electrostatic interactions and we are going to test the effect of the ionic strength on the stability of this dispersion. On the other hand, as dispersed particles contain charged surface groups we also anticipate an influence of the metal walls of the ring-slit die on the flow induced aggregation. In order to investigate this effect we cover the ring-slit die walls with a thin PTFE film.

We have also tested the effect of particle deformability on the aggregation phenomenon of the soft polyurethane and hard polystyrene particles. The results show a similar behaviour of both dispersions in the ring-slit test.

This work provides insight into the contribution of different phenomena to the aggregation in strong extensional flows. Reported results are an important first step in understanding the mechanism of flow induced aggregation of highly concentrated dispersions.

4   Literature

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