Controlled structuring of dispersed food systems

Peter Fischer, Carsten Cramer, Erich J. Windhab, Bernhard Walther*, Lars Hamberg*, and Anne-Marie Hermansson*

ETH Zurich, Laboratory of Food Process Engineering, Institute of Food Science and Nutrition, 8092 Zürich, Switzerland

*SIK – The Swedish Institute for Food and Biotechnology, P.O. Box 5401, 402 29 Göteborg, Sweden

ABSTRACT

Dispersed systems such as emulsions and suspensions are encountered in a large variety of applications areas such as food, cosmetics, pharmaceutics and polymers. To obtain the desired performance of an emulsion the dispersing process, i.e. droplet size distribution has to be monitored and controlled. By combining droplet generation, deformation and fixation in one experimental set-up we aim to produce equally shaped particles in order to manipulate the mircostructure of dispersions. In a first step we study a co-flowing liquid-liquid emulsification process aiming to generate monodispersed droplets¹⁻². With such droplets at hand, deformation of each individual droplet can be achieved in a second step when the flow field of the downstream apparatus is known. Using gelling biopolymeric material as dispersed phase it is further possible to "freeze" and conserve the non-equilibrium shapes of such deformed droplet. As a consequence, suspensions of gelled emulsion droplets of various shape and shape functionality were obtained³⁻⁵. These new shapes (sphere, fibrils, "hooky" bodies) provide an advanced tool to control and manipulate the flow properties and product performance of dispersed systems beside the well-known influence of the volume fraction of the dispersed particles^{4, 6}.



drop generation drop deformation drop fixation Figure 1. Generation, deformation and fixation of a gelling biopolymer droplet toward a shaped suspension particle.

INTRODUCTION

The goal of this work is the continuous production of tailor-made droplets in size and shape in order to manipulate the microstructure of the dispersion. To achieve this the flow kinetics, fixation kinetics and kinetics at the interface (e.g. surfactant adsorption) have to be coupled (Fig. 1). Flow processes are used to deform liquid emulsion droplets on their way to suspended gelled particles and thus imprinting liquid-liquid deformation onto solid particles.

In this investigation drop generation, drop deformation and gel kinetics are combined in a fast continuous flow process to study the impact of shear and elongation forces on drop deformation with and without simultaneous gel formation under high temperature gradients. Drops are generated in a double capillary and deformation and superimposed gel formation occurs along a narrowing deformation channel.

Droplet Generation

To produce emulsions well-established dispersing devices are commonly used where droplets are subjected to shear and elongational stresses and fragmented into smaller droplets. Generally, the dispersed droplets display a certain size distribution and enormous effort has to be undertaken to achieve narrow size distributions⁷. The demand for almost monodisperse emulsions has been rising due to the production of microcapsules or specially structured multiphase systems. Modern dispersing techniques such as membrane emulsification represent an example of a direct production technique of emulsions where the polydispersity lies in the range of 10% of the average droplet size⁸. In microchannel emulsification, poly-dispersities of droplets below 5% was achieved with the droplet size depending primarily on the capillary size and channel geometry⁹.

Another dispersing technique is realized by injecting the disperse phase via a capillary into the continuous phase^{10, 11}. It is distinguished into two different drop generation mechanisms: Either the drops break up at the capillary tip (dripping) or they are generated from an extended fluid jet (jetting)^{1, 2, 11}. The fundamentals of dripping and jetting have been investigated extensively but these drop formation mechanisms have rarely been considered as a promising dispersing tool with relevance for technical applications.

In the present work, the disperse phase is injected via a needle into a flowing ambient continuous phase as shown in Fig. 1 (drop generation). The droplet breakup from the capillary tip is promoted by the drag force of the continuous phase in comparison to the injection into a quiescent surrounding fluid. Thus, the material properties, such as interfacial tension, γ , viscosities, η_{cont} , η_{disp} , and density of the fluids are not the only governing parameters but the droplet size, d_{drop} , is rather controlled by the velocity of the continuous phase, v_{cont} , and the needle diameter, d_{cap} . An integral force balance accounts for the drag force of the flowing ambient fluid and the interfacial tension force (right side) [12]:

$$3 \cdot \pi \cdot \eta_{cont} \cdot v_{cont} \cdot \left(d_{drop} - d_{cap} \right) = \pi \cdot \gamma \cdot d_{cap}$$
(1)

The drag force (left side) was calculated according to a modified version of the Stokes formula for a solid sphere. Even though this model is considered as an approximation, Umbanhowar and co-worker found good agreement between theoretical predictions and experimental data by introducing a fitting parameter¹².

Droplet Deformation

In contrast to solid particles, droplets are deformable in flow when they are subject to stresses. The generated stresses depend on the geometry of the flow device, the drop's trajectory in the flow and the strength of the flow. In the present study the droplets are injected eccentrically into a narrowing flow channel. The flow stresses are controlled by the position of the injection point of the droplets into the channel and by the flow rates of the phases. In Fig. 1 (drop deformation) the droplet is deformed in shear flow on a well-defined streamline which is determined by the injection point. As a consequence, all droplets follow the same streamline and experience same stresses. Therefore, the deformation history of all droplets is identical under steady flow conditions along the flow channel. A welldefined, predictable deformation of the droplets is desired to investigate the influence of the particle shape on the product properties.

The deformation of the droplet is described most conveniently by the Taylor deformation theory. When a droplet is subjected to a shear-rate, $\dot{\gamma}$, it deforms from the initial spherical shape into an ellipsoidal one if the deformation is small. After initial transients have decayed, the droplet reaches a steady state deformation which is the result of an equilibrium between viscous forces, which tend to deform the droplet and even break it if they are large enough, and interfacial forces, which attempt to recover the initial state А dimensionless deformation parameter, D, characterizes the deformation of the droplet as:

$$D = \frac{a-b}{a+b} \tag{2}$$

where a is the major and b is the minor axis of the fitted ellipse. For small deformations, the steady-state geometry of the droplet can be described using Taylor theory:

$$D = Ca \frac{19\lambda + 16}{16\lambda + 16} \tag{3}$$

where λ is the ratio of the disperse phase viscosity to the continuous phase viscosity. *Ca* is the capillary number defined as:

$$Ca = \frac{\eta_c \dot{\gamma} a}{\gamma} \tag{4}$$

The Taylor equation is valid for systems in which both fluids are Newtonian, the deformations are small and the viscosity ratio is close to unity¹³.

Droplet Fixation

Because of the interfacial tension between the immiscible liquids the droplets lose their imprinted deformation as soon as they enter an area of zero stress in the flow channel or for example during storage of the dispersion. By superimposing a drop fixation step to the drop deformation process, drop shapes can be conserved¹⁴. Droplet fixation may be induced by physical or chemical reactions within the disperse fluid. For example, gelation takes place when a heated emulsion of a gel-forming cold-set biopolymer is cooled below a specific temperature as shown in Fig. 1 (drop fixation).



Figure 2. Droplet generation in a co-flowing environment.

EXPERIMENTAL

Flow Cells

The droplet generation cell to study the impact of process and material parameters on the drop formation in a co-flowing ambient fluid is illustrated in Fig. 2. A steady, non-pulsating flow of the continuous phase was generated using a gear pump (Ismatec MCP-Z Standard). The disperse phase was injected via a capillary into the flow channel using a syringe pump (Hamilton Microlab 500 series) whose drainage rate is controlled. The injection point of the disperse phase was placed at the centreline of the channel where the velocity of the continuous phase is at a maximum. The evaluation of the experiments relied on the use of a drop-counting apparatus in which a laser beam is interrupted whenever a drop passes the beam's path (New Focus, Model 2001-FS). Additionally, the drop breakup was observed using a moveable CCD-camera (Sony DFW-V500) equipped with a macrozoom lens (Computar TEC-M). All experiments for the droplet generation studies were carried out at room temperature $T = 22^{\circ}C$ with non-gelling biopolymers.

The droplet deformation and fixation cell is shown in Fig. 3. In this set-up the droplet generation tool describes before is used as injection tool of the monodispersed droplets. In the downstream channel, the droplets are subjected to a contracting flow imprinting the deformation. When fixation is superimposed gelled droplets are obtained at the end of the deformation cell (right image of Fig. 3).



Figure 3. Injection tool and shaping flow cell.

Materials

The experiments were carried out using refined sunflower oil (SFO) as continuous phase with a measured viscosity of 0.049 Pas. As disperse phase either aqueous solutions of gelling and non-gelling κ -carrageenan or aqueous solutions of polyethylene glycol (PEG) were used. The weight fraction of κ -carrageenan in the solution was varied from 0.1 to 1.5% to study the effect of different viscosities of the disperse phase on the drop formation^{2,14}.

RESULTS AND DISCUSSION

Droplet Generation

The droplet generation in the dripping regime is depicted in Fig. 4 for different

velocities of the continuous phase. The process can be characterized by stretching of the neck, detachment of the primary droplet, and finally generation of smaller satellite droplets.



increasing velocity of continuous phase

Figure 4: Droplet generation in the dripping regime.

The influence of both the velocity of the continuous phase and its viscosity is shown in Fig. 5.



Figure 5. Droplet diameter as a function of velocity and viscosity of the continuous phase.

Increasing both parameters will lead to decreased droplet diameters at a fixed flow rate of the dispersed phase. It is interesting to note that the droplet diameter is not affected when the viscosity of the dispersed phase is increased a constant velocities of the dispersed phase. Only the formation of the neck becomes more and more pronounced with increasing viscosity, η_{disp} , as shown in Fig. 6.



The influence of the interfacial tension on the droplet diameter is studied in Fig. 7. Since the interfacial tension is the only conservative force in the force balance (Eq. 1) increasing values of γ will lead to longer residence times at the needle's tip and consequently to larger droplets. As shown in Fig. 7 the smallest droplets are achieved with the system PEG/SFO exhibiting an interfacial tension of 8 mN/m. The same effect is reflected by force balance given by the Capillary number (see next section).



Figure 7. Influence of the interfacial tension of the droplet diameter.

The production of micro-sized droplets in a co-flowing environment is summarized in Fig. 8 where both flow regimes, dripping and jetting are displayed. Droplet diameter of

less than 50 μ m and droplet numbers of up to several thousand per second can be achieved. The polydispersity lies in the range of 1 - 2%.



Figure 8. Generation of small droplets in coflowing environment.

Droplet Deformation

The deformation of a droplet travelling on a streamline in the contracting channel geometry is shown in Fig. 9. In the beginning, the deformation, *D*, is around 0, reflecting the spherical shape of the droplet.



Towards to contraction, D increased and eventually relaxes when the droplet enters the straight outlet channel. To obtain a sufficient deformation of the final particle, gelation has to take place at the highest deformation, i.e. at the 170 - 180 mm position of the channel. According to the Taylor theory (Eq. 3) the droplet diameter should not influence the deformation parameter as seen in Fig. 10. It is surprising that in the unsteady flow situation present in the contraction flow the model is working fine for a wide range of capillary numbers.



Figure 10. Deformation of different droplet sizes in a contraction flow.

Droplet Fixation

Superimposing a gelation process initiated by a temperature quench will fix the droplet's shape at its highest deformation in the flow channel. Restricted by the residence time, the gel point of the biopolymer, and the heat transfer the fixationprocess has to be timed exactly.



Figure 11. Deformation of a temperature quenched biopolymer droplet above and below the gel temperature.

As measure for the successful gelation the deformation parameter, D, was used. As long as D retracts to zero the gelation did not took place. Once the deformation is constant in time, gelation was successfully applied to a deformed emulsion droplet. In Fig. 11 the deformation of a droplet travelling along the contracting channel (length expressed as capillary number, Ca) at different temperatures of the continuous phase is shown. As long the temperature is above the gel temperature the full deformation is achieved (T = $29 - 35^{\circ}$ C). As soon as gel formation (T = $26 - 28^{\circ}$ C) is induced the strongly increasing viscoelasticity of the drops starts to decrease deformation. The increase of the dispersed phase viscosity plays a minor role and cannot supply enough stresses to maintain the deformation (Eq. 4). Upon further cooling of the continuous phase, deformation decrease due to the higher temperature gradient between the phases that is causing faster gelling or an earlier onset of gel formation. It is interesting to note that the formation of a gel network is delayed until the continuous deformation phase has a temperature of 26°C. Under this condition the system is sufficiently quenched to induce network formation in the drops early in the deformation channel where the shear stresses, provoking internal flow and disruption of developing networks, are low.

In comparison to the deformed particles in Fig. 12 that were produced in a four-roll mill the deformation and shape of the particles produced here are smaller and less fancy³. Comparing both techniques, strong elongational flow (large and increasing *Ca* number during the process) and moderate shearing flow (moderate *C a* numbers), suggest the use of high viscous continuous phases and complex flow geometries.

Additionally the results showed that drop deformation and gel formation in the described flow process can be used as a novel method to measure gel kinetics under high temperature gradients and short time scales.



Figure 12. Shape class of deformed droplets in high capillary number flow³.

CONCLUSIONS

The present study has shown the possibility to deform emulsion droplets that were produced in a co-flowing environment into ellipsoids in a downstream deformation channel. The mechanisms to produce, deform and fixat the emulsion droplet, i.e. the suspension particle, was presented, discussed and now can be scaled up to a small producting device as shown in Fig. 13.



Figure 13. Droplet generation, deformation, and fixation cell.

An in-situ method to study the impact of temperature-induced gel formation on drop deformation along the deformation channel was presented. This method gives the opportunity to study gel kinetics on short timescales under high temperature gradients.

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REFERENCES

- [1] Cramer C, Fischer P, Windhab EJ: Liquid jet stability in a laminar flow field, Chemical Engineering and Technology 25 (2002) 499-505.
- [2] Cramer C, Fischer P, Windhab EJ: Drop formation in a co-flowing ambient fluid, Chemical Engineering Science, in press.
- [3] Walther B, Walkenström P, Hermansson A-M, Fischer P, Windhab EJ: Flow processing and gel formation: A promising combination for the design of the shape gelatin drops, Food Hydrocolloids 16 (2002) 633-643.
- [4] Walther B, Hamberg L, Walkenström P, Hermansson A-M: Formation of shaped drops in a fast continuous flow process, Journal of Colloid Interface Science 270 (2004) 195-204.
- [5] Hamberg L, Wohlwend M, Walkenström P, Hermansson A-M: Shapes and shaping of biopolymer drops in a hyperbolic flow, Food Hydrocolloids 17 (2003) 641-652.

- [6] B. Wolf B, Frith WJ, Singleton S, Tassieri M, Norton I: Shear behaviour of biopolymer suspensions with spheroidal and cylindrical particles. Rheologica Acta 40 (2001) 238-247.
- [7] Bibette J, Leal-Calderon F, Schmitt V, Poulin P: Emulsion science, Springer, Berlin (2002).
- [8] Yuyama H, Yamamoto K, Shirafuji K, Nagai M, Ma GH. Omi S: Preparation of polyurethaneurea uniforme spheres by SPG membrane emulsification technique, Journal of Applied Polymer Science 77 (2000) 2237-2245.
- [9] Sugiura S, Nakajima M, Seki M: prediction of droplet diameter for microchannel emulsification, Langmuir 18 (2002) 3854-3859.
- [10] Basaran OA: Small scale free surface flows with breakup: Dropl formation and emerging applications, AIChE Journal 28 (2002) 1842-1848.
- [11] Cramer C: Continuous drop fomation at a capillary tip and drop deformation in a flow channel, ETH Dissertation 15460, Zurich/Switzerland (2004).
- [12] Umbanhowar PB, Prasad V, Weitz DA: Monodispersed emulsion generation via drop break off in a coflowing stream, Langmuir 16 (2000) 347-351.
- [13] Megías-Alguacil D, Fischer P, Windhab EJ: Experimental determination of interfacial tension by different dynamical methods under simple shear flow conditions with a novel computercontrolled parallel band apparatus, Journal of Colloid and Interface Science 274 (2004) 631-636.
- [14] Walther B, Cramer C, Hamberg L, Fischer P, Hermansson A-M, Windhab EJ: Drop deformation dynamisc and gel kinetics in a co-flowing water-in-oil system, submitted.