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Emulsification of particle loaded droplets with regard to miniemulsion polymerization

Lena L. Hecht [a,*,1], Tobias Merkel [a,1], Alexander Schoth [b,2], Caroline Wagner [b,2], Karsten Köhler [a,1], Rafael Muñoz-Espí [b,2], Katharina Landfester [b,2], Heike P. Schuchmann [a,1]

[a] Karlsruhe Institute of Technology, Institute of Process Engineering in Life Sciences, Section I: Food Process Engineering, Kaiserstraße 12, 76131 Karlsruhe, Germany
[b] Max Planck Institute for Polymer Research, Ackermannweg 10, D-55128 Mainz, Germany

HIGHLIGHTS

- Production of hybrid particles requires break-up of particle loaded droplets .
- Agglomerates hinder droplet break-up.
- High pressure homogenization can successfully break-up particle loaded droplets.
- HPPF-process can be used to avoid abrasion on high pressure pump and disruption unit.
- Adjusting surfactant concentration leads to final product of high homogeneity.

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ABSTRACT

Composite nanostructured particles can be produced by polymerization of particle-loaded miniemulsion droplets. Breaking-up particle-loaded droplets is a challenge, because an increased viscosity and abrasiveness of the droplets has to be handled. Additionally, agglomerates in the droplets hinder their deformation and break-up and lead to large, non-spherical droplets. In this article, we show that high pressure homogenization is a promising process. If agglomerates are eliminated, droplets with encapsulated inorganic nanoparticles can be broken up to small sizes (here, droplets with 50 wt.% silica nanoparticles to sizes below 300 nm). Abrasion on the high pressure pump and the disruption unit can be avoided using a high pressure post feeding valve.

In miniemulsion polymerization the surfactant concentration has to be adjusted to avoid secondary nucleation, which would result in the formation of unfilled plain polymeric particles. The required surfactant concentration is influenced by the particle load, in particular by particle surface-functionalizing molecules. To eliminate this, the surface modification of the nanoparticles was adjusted. Thus, homogeneous hybrid particles could be prepared.

1. Introduction

Hybrid nanoparticles have been of ongoing interest for academy and industry in the last years. They can be used for various applications, from paints of high color intensity [1–3] over electronic devices [4,5] to medical applications [6–8].

Miniemulsion polymerization is a technique often used for the preparation of hybrid particles. Usually, a two-stage process is applied [9–11]: first, a nanoparticle-in-monomer suspension is emulsified in a continuous phase; second, the polymerization of the filled submicron-sized monomer droplets is conducted by miniemulsion polymerization.

In miniemulsion polymerization, droplet nucleation is the dominant nucleation mechanism. Initiator molecules start the polymerization reaction in the droplet and chain growth also takes place in the droplet, acting as a "nanoreactor". As a result, the droplets keep their identity: the mass stays constant, as well as the number of particles [12]. With regard to hybrid particles, this is a big advantage as the inorganic compound can be dispersed in the droplet and the composition of the droplet can be kept constant during polymerization. In this way, one-core to multi-core composite particles, as well as raspberry-like structures, can be produced.

The structure of the hybrid particles depends on the particle surface. To encapsulate the nanoparticles in the monomer, their

* Corresponding author. Tel.: +49 721 608 42497; fax: +49 721 608 45967.
E-mail address: lenahecht@kit.edu (L.L. Hecht).
[1] Tel.: +49 721 608 42497.
[2] Tel.: +49 6131 379 170.

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surface has to be lipophilic. Hydrophilic nanoparticles can be functionalized by either physical modification (adsorption of a surfactant on the particle surface) [13] or by chemical modification. An often used chemical modification method is the treatment of silica particles with the coupling agent 3-methacryloxypropyltrimethoxysilane (MPS) [10,14]. Due to the modification with MPS the hydrophobic monomer adsorbs on the silica surface and, further on, the methacrylate groups promote the formation of polymer around the core by polymerization of the olefinic groups [14,15].

The preparation of hybrid nanoparticles via miniemulsion polymerization has been investigated by many research groups, focusing especially on the morphology of the particles [16,17]. Encapsulation of high particle concentrations, however, is still challenging. With increased particle load, broad particle size distributions [18] result and the mean particle size increases [15,19,20].

As the droplet size distribution adjusted in emulsification directly determines the final product properties, the emulsification step is of great importance. If the surfactant concentration is sufficiently high to stabilize the miniemulsions against coalescence, the monomer droplet size is defined by the droplet break-up [21,22]. Droplet deformation and disruption depends on the intensity and duration of the deforming viscous stresses and the shape conserving interfacial and viscous stresses. It can be characterized by the capillary number (Ca) [23,24]:

$$Ca = \frac{\tau \cdot d}{2 \cdot \gamma} \quad (1)$$

τ is the shear stress, γ is the interfacial tension and d the droplet diameter. Under a critical value of the capillary number Ca_{crit} droplets are only deformed, whereas over this value droplets are disrupted. The critical capillary number depends on λ the ratio between the viscosity of the dispersed phase and the continuous phase. λ influences the droplet break-up in dependence of the flow regime: For simple shear flow, smallest droplet sizes can be achieved for a viscosity ratio between $0.1 < \lambda < 1$. No break-up is possible for $\lambda > 4$, because the droplets start to rotate [25,26]. For elongational flow, droplets with a significantly higher viscosity ratio can be broken up [25]. For turbulent flow the droplet break-up starts to deteriorate if the viscosity ratio rises above $\lambda = 10$ [27].

Droplet break-up also depends on the energy density E_V applied to the emulsion [28]. E_V is defined as the power input P divided by the flow rate of the emulsion $\dot{V}$ [28] and is thus a value characterizing the mean value of all stresses applied to the droplets in the emulsification step.

Technical processes known to disrupt droplets are ultrasonic devices, high pressure homogenizers, rotor–stator systems, and static mixers. While in general all processes can be used to prepare miniemulsions, high pressure homogenizers are very likely the most suitable devices to produce small droplet sizes at a high throughput. The main components of a high pressure homogenizer are a high pressure piston pump, which creates a pressure of 100–5000 bar, and a homogenization unit, being composed mainly of a narrow gap in which the fluid is accelerated up to velocities of several hundreds of m/s [29]. Stresses responsible for droplet break-up result from simple shear, elongational shear, turbulent fluctuations, and cavitation [30].

High pressure homogenization has been rarely used to prepare miniemulsions up to now. For moderate viscous dispersed phases (η_d = 112 mPa s), high pressure homogenization with a flat valve was applied. With several passages at a pressure of up to 414 bar, droplet sizes below 100 nm could be reached [31,32]. By using an additional static mixer, Goikoetxea et al. [33] could reduce the number of passages necessary to reach that size. Jeong et al. emulsified Kraton rubber/styrene droplets with a flat valve and reached extremely broad droplet size distributions (20 nm to 2 μm). Unfortunately, the viscosity of the dispersed phase is not stated in this article [34].

To our knowledge, no results regarding the break-up of higher viscous droplets or nanoparticle loaded droplets by high pressure homogenization have been published.

Usually with increasing particle load, particle suspensions show an increase in viscosity and a shear thinning or viscoelastic behavior [35]. Ultrasonication has been used to emulsify particle loaded droplets and an increase in droplet size has always been observed [15,19,20]. Usta et al. simulated the influence of nanoparticles on droplet deformation and observed a decreased deformation for an increased particle load [36]. Bourgeat-Lami et al. observed particle loaded miniemulsions via cryo-TEM. The nanoparticles were located at the droplet surface and many small, unfilled monomer droplets were found in the samples. The authors conclude that unfilled droplets or areas of droplets break-up easier and thus result in smaller droplets. The size of the encapsulated nanoparticles (20 nm vs. 78 nm) had no influence on the resulting droplet size [15].

Regarding the emulsification of non-Newtonian fluids without particle load, various publications can be found. The break-up of visco-elastic droplets has been investigated theoretically as well as experimentally: It can be summarized that visco-elastic effects reduce droplet deformation and droplet disruption [36,37]. Regarding shear-thinning droplets, the deformation and disruption of the shear-thinning droplets is increased if the zero-shear-viscosity is compared [38]. If the viscosity at the shear rate during droplet break-up is considered, the deformation and break-up of the shear-thinning droplets is similar [39–41] or reduced [42,43] in comparison to Newtonian droplets.

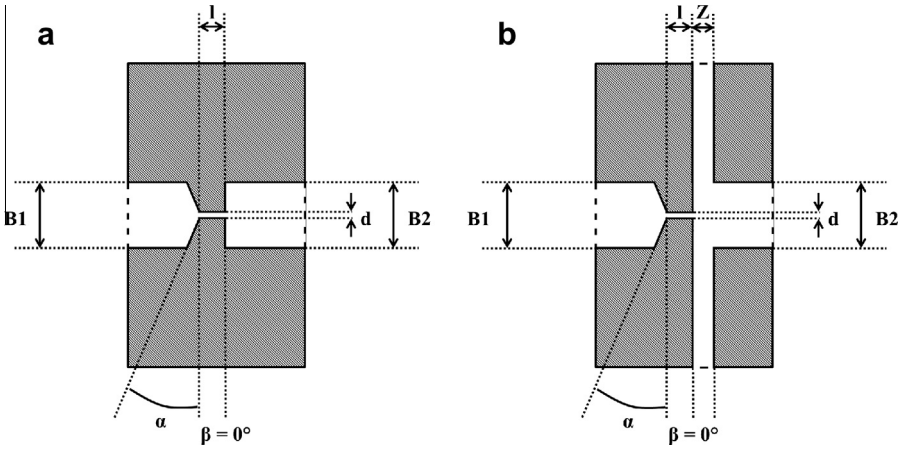

Fig. 1. Geometry details of (a) an orifice valve and (b) a high pressure post feeding (HPPF) valve.