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Miniemulsification by catastrophic phase inversion

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ABSTRACT

We present an alternative method for the preparation of high solids content, water-borne latex products from a combination of catastrophic phase inversion (CPI) and miniemulsification. Miniemulsions are commonly prepared by the direct emulsification of a monomer in water and subsequent miniemulsification using a high-shear technique. Herein high solid content dispersions of up to 80 w/w% solids content monomer-in-water emulsions are prepared by catastrophic phase inversion followed by miniemulsification with a rotor-stator mixer. The subsequent miniemulsification of these monomer-in-water emulsions proves to be almost four times more energy efficient than is possible with direct miniemulsification using the same mixers and recipes. The highly concentrated miniemulsions thus obtained can be successfully diluted to different solid contents for polymerisation, without compromising the droplet size distribution, and used to produce colloidally stable latexes.

1. Introduction

Traditionally the majority of free radical polymers have been made by suspension and conventional emulsion polymerisation. However, over the course of the past decade, miniemulsions have recaptured the attention of both academics and industrial producers of polymers because of the ease with which one can incorporate a wide range of organic and inorganic materials into the final polymeric product. In addition the ability to directly emulsify dispersions with solids contents of up to 50, or even 60 volume per cent have made miniemulsions increasingly attractive as a means for production of heterogeneous aqueous dispersions of polymer particles [1,2]. Monomer-in-water miniemulsions are typically generated by the direct emulsification of monomer (referred to as the oil phase, O) and water (W), followed by subsequent miniemulsification. The monomer in water emulsions (O/W) tend to follow Bancroft's rule [3], i.e. the phase in which the surfactant is most soluble will act as the continuous phase, and consequently a continuous aqueous phase with dispersed monomer droplets ($\sim$0.1–5 μm depending on surfactant and agitation conditions) is obtained during direct emulsification.

Miniemulsions are usually generated by mechanical homogenisation of an O/W mixture to reduce the droplet size to the miniemulsion range ($\sim$50–500 nm) using some form of intense mixing such as rotor stator mixers [4], high pressure homogenisers [5] or static mixers [6]. For instance, El-Jaby et al. showed that it could take well over one hour to create polymerisable miniemulsions using a rotor stator mixer [4]. A reduction of this emulsification time could lead to more commercially useful processes.

Typically, miniemulsification processes lose significant amounts of energy to heat, reversible rupture and droplet coalescence and as a consequence only a small fraction of the mechanical energy is effectively used for droplet size reduction (an exception to this is the use of static mixers, which appear to be less prone to heat losses). Therefore, one of the major challenges that face the generation of miniemulsions on industrial scale is high energy consumption, and until recently, the need for high shear to produce droplets of appropriate size [4]. From this point of view, the phase inversion method could provide a promising alternative for the generation of miniemulsions [7].

Phase inversion is a method that can be used for emulsification, when a change in the free energy of a water-in-oil (W/O) emulsion causes it invert to an oil-in-water (O/W) emulsion or vice versa [8]. There are two types of phase inversion: (i) transitional phase inversion (TPI) [9–13] and (ii) catastrophic phase inversion (CPI) [14–23]. During TPI the emulsion inverts due to a change in the affinity of the surfactant(s) for either phase, quantified by the hydrophilic–lipophilic balance (HLB) of the surfactant. A change in the HLB value of the surfactant can be achieved by changing either the surfactant composition or changing the temperature. CPI typically describes an inversion process where an abnormal emulsion (i.e. an emulsion in which the surfactant has a greater affinity for the dispersed phase) inverts to a stable emulsion. Abnormal emulsions do not obey Bancroft's rule and therefore are highly unstable [8]. CPI can be achieved by either increasing the volume fraction of the dispersed phase by the gradual addition of the surfactant-soluble dispersed phase to the continuous phase or simply by adding the

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dispersed phase instantaneously followed by continuous agitation [8,19]. Upon addition of the dispersed phase small inclusion droplets are formed within it, resulting in a double emulsion [22]. This is a process referred to as "internal-phase-emulsification". The inclusion of smaller droplets occurs until the internal phase droplets approach the critical closed packing value, and then the system suddenly and irreversibly inverts [19]. However, as we will see below, the instantaneous addition of the dispersed phase for CPI can only be used until a limiting solids content, below which direct emulsification is likely to occur.

CPI as an emulsification method has received recent interest for its ability to produce emulsions at high solids content (≥50 w/w%) with droplet sizes on the order of microns [14–23]. Moreover, CPI is an industrially relevant technique for preparation of paints, construction materials and polyurethane dispersions [7,24]. When compared to direct (or conventional) emulsification, CPI typically generates smaller droplet sizes and less energy is required to produce droplets of a given size [22,25,26]. In addition, the efficiency of the CPI processes only increases with increasing solids content, e.g. an increasing amount of oil phase. However, as CPI can only produce droplets in the micrometer range, mechanical homogenisation devices, such as static mixers [6], rotor stators [4], or sonication devices [1] are still required if droplets in the miniemulsion size range (100–500 nm) are desired.

This paper explores the potential of producing high solid content miniemulsion-based latexes from the combination of catastrophic phase inversion, subsequent miniemulsification and polymerisation. To the best of our knowledge, this combination of techniques has not been used previously, and, as we will show, it clearly has the potential to reduce both the time and energy consumption for miniemulsification. The CPI technique is applied here to generate high solids content O/W emulsions, where the oil phase consists of a polymerisable monomer and co-stabiliser for the miniemulsification process. Subsequently the O/W emulsions are subjected to mechanical homogenisation to generate stable polymerisable miniemulsions. Our results show that CPI in combination with simple mechanical homogenisation is a promising route to obtain high-solids content latex-based products in a commercially viable manner.

2. Materials and methods

2.1. Chemicals

The monomer methyl methacrylate (MMA, Aldrich, 99%) and co-stabiliser octadecyl acrylate (ODA, Aldrich, 97%) were used as received. The surfactants sodium dodecylbenzene sulphonate (SDBS, Acros Organics, 88%), Disponil A3065 (Cognis, 65 w/w% solution in water), sodium dodecyl sulphate (SDS, Acros Organics, 99%), stearic acid (SA, Aldrich, reagent grade), potassium hydroxide (KOH, Aldrich, reagent grade) and initiator potassium persulfate (KPS, Acros Organics, <99%) were used as received. For all experiments distilled deionised water (DDW) is used, purified by a Millipore Synergy ion exchange unit.

2.2. Apparatus

The rotor stator emulsifications were carried out in a 1 L jacketed glass vessel with a 12 cm diameter. The vessel had two equally spaced cylindrical glass baffles 3/8″ in diameter, and was cooled with tap water. The VMI Rayneri Turbotest rotor stator with a 4-blade 5.5 stator head was used as the mixing device. Polymerisations are performed in a jacketed 1 L reactor with a 4.25″ diameter. The reactor contents were mixed by an Arrow 1750 mixer. A Caron 2050 W Heater was used to heat the water cycling through the jacket of the reactor to 70 °C. A nitrogen tank was connected to the reactor for purging and a condenser with a bubbler attachment was fixed to the top of the reactor.

The conductivity was measured with a CDM210 conductivity meter. All viscosity measurements were performed with a Brookfield DV-E Viscometer using either the s62 or s64 heads. Droplet and particle size distributions were determined using the Malvern Mastersizer 2000. The uniformity, which is a measure of the absolute deviations from the median particle diameter, is a measure of the width of the droplet and particle size distribution as calculated by the Malvern software. The lower the value of the uniformity, the more monodisperse the sample.

2.3. Catastrophic phase inversion

For a typical experiment at a solid content of 60 w/w% (i.e. 60 wt% organic phase, 40 wt% aqueous phase) and a surfactant concentration of 3 w/w% SDBS with respect to monomer, the organic phase was prepared by dissolving ODA (35 g, 7.0 w/w% with respect to monomer) in MMA (500 g) and the aqueous phase by dissolving SDBS (15 g) in distilled deionised water (350 g). The organic phase was placed in the tap water-cooled rotor stator vessel with the rotor stator head rotating at 50 rpm and the entire aqueous phase was added to start the emulsification. During the emulsification, the rotational speed was altered between 50 rpm and 250 rpm every minute; trial and error showed that alternating rotational speeds led to faster phase inversion. The reasons for this are not clear, and an in-depth exploration of this observation will be left for a future study. The conductivity was monitored continuously to follow the phase inversion process. Phase inversion was considered to occur once there was a significant increase in conductivity (∼1.4 mS/cm for the SDBS surfactant emulsions). Subsequently, the rotational speed was set to 500 rpm to avoid separation of the components. After 10 min of agitation, the droplet size distribution and the viscosity were measured.

2.4. Miniemulsification

The phase-inverted O/W emulsions were agitated at 3000 rpm using the rotor stator and the droplet size distributions were measured periodically to monitor the progress of the miniemulsification process.

2.5. Miniemulsion polymerisation

All polymerisations are performed at 70 °C in a 0.25 dm^3 glass three-necked round-bottom flask equipped with a teflon impeller, reflux condenser and nitrogen purge line. A typical polymerisation was performed as follows: 80 g of a 70 w/w% miniemulsion was diluted with 84 g of an aqueous SDBS solution at the critical micelle concentration (CMC, 2.8 mM at $T = 293$ K) [17] to the desired solids content of 40 w/w%. Subsequently, the diluted miniemulsion was transferred into the round-bottom flask and purged with nitrogen for 15 min. Concurrently, an initiator solution consisting of KPS (0.11 g, 0.44 mmol) in DDW (5 g) is prepared and purged with nitrogen. The initiator solution is added to the miniemulsion to initiate the polymerisation. Samples are withdrawn periodically to monitor the conversion by gravimetry and the droplet/particle size distribution by dynamic light scattering.

3. Results and discussion

3.1. Catastrophic phase inversion

In this paper the initial continuous phase (oil phase, O) consists of the monomer methyl methacrylate (MMA) and octadecyl