Emulsification for Latex Production Using Static Mixers

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Summary: Evolution of droplets generated by static mixers have been investigated in terms of surfactant concentration, flow rate through the pump, monomer hydrophobicity and the type of static mixer. Operating at faster pump flow rates and using the PAC static mixers generated smaller miniemulsion droplets. Similar effects were observed at higher surfactant concentrations (3.0 vs. 1.0 g/L) and using monomers of increasing hydrophilicity (MMA vs. St). When comparing the efficiency of PAC static mixers to SMX mixing elements it was found that SMX was capable of generating droplets approximately 100 nm smaller at similar pump flow rates in the same time period. Based on these promising results, the SMX mixers were further evaluated based on surfactant concentration. The miniemulsion droplets were polymerized and their distribution was evaluated.

Keywords: emulsification; miniemulsion polymerization; miniemulsion; SMX; static mixers

Introduction

Miniemulsion polymerization introduces a fresh new outlook on latex production due to its functional versatility and ability to incorporate organic and inorganic compounds. This allows creating of novel latices using the same basic materials as in emulsion technology.[1] Miniemulsion droplets with diameters typically of the order of 50–500 nm are created by mechanically dispersing an organic phase in an aqueous medium using a mechanical homogenizer coupled with a well-adapted stabilization system. The organic phase consists of a monomer and hydrophobic costabilizer which reduces the rate of Ostwald ripening.[2] The aqueous phase typically contains an anionic, cationic or non-ionic surfactant or their blend. In the case of radical polymerization, the initiator can be either water-[3] or oil–soluble.[4] The polymerization proceeds in such a manner that the monomer droplets are converted directly to polymer particles. In an 'ideal' miniemulsion, every monomer droplet is converted to a polymer particle.

The need for an efficient mechanical homogenizer is a deceivingly important concept in the generation of miniemulsion droplets. Without the production of narrowly monodisperse miniemulsion droplets (in addition to a suitable stabilization system), the nucleation method can veer from 'ideal' and, in doing so, loses all the inherent advantages of a miniemulsion system. One of the more common devices, ultrasonication (US) was and still is the preferred device because of its simple operating procedure and relative ease of use. However, on the laboratory scale US appears to be restricted to volumes of 0.025–0.25 L. More recently, high-pressure homogenisers (HPH) (which are used in a number of industrial applications) have been implemented and have shown that they can be an effective means of

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emulsifying larger volumes (0.25–0.5 L) of miniemulsions. They are convenient, generating droplets of hundreds of nm within minutes, but are energy-demanding and sometimes require a prehomogenization step to be viable.[5] Previous work of our research group investigated the feasibility of rotor-stators (which are currently used in industrial dispersion applications) as emulsification devices.[6,7] It was found that the rotor-stator required more time than US to generate droplets (minimum 60 min). Its major advantage is the capability of homogenizing a much larger volume (1–2 L) than US.[7]

Static mixers are another device believed to have a significant industrial potential. While static mixers are widely used in other agro- and petrochemical processes, they have not been studied in depth for the generation of miniemulsion droplets. It is clear that they can be economically practical, safely used and can be utilized on larger scales. However, in terms of dispersion systems, their role in droplet breakage is an area of ongoing research. Preliminary investigations by Ouzineb et al. showed that simple static mixers are viable alternatives to rotor-stators and ultrasound due to their low energy consumption and relatively low shear that they impose on the phase being dispersed.[6] It was found that only a small amount of the total energy required to operate static mixers is consumed for droplet breakage (1–4%); the rest is lost being converted to heat and coalescence. This can be improved, but they still compare favourably with efficiencies of 0.002–0.007% for rotor-stators and sonication reported in the original study. The authors also investigated the effect of varying monomers of different hydrophobicities on droplet size. They generated droplets of various sizes when monomers with different interfacial tension values (a function of hydrophobicity) are subjected to the same amount of work done by the homogenization device (Eq. 1).

$$\Delta A = W_{\text{breakage}} \times (\gamma)^{-1} \qquad (1)$$

where W_{breakage} is the work done by the homogenization device, γ is the oil-water interfacial tension and ΔA is the droplet surface area. For a given amount of work applied to a monomer with a low interfacial tension (methyl methacrylate) compared to one with a higher interfacial tension (styrene), a larger surface area results (smaller average droplet size) for the system containing monomer of lower interfacial tension.

Ouzineb et al. introduced and showed that static mixers are a plausible means of generating miniemulsion droplets;[6] however, they did not explore the role of different process conditions such as flow rate and surfactant concentration. Therefore, building on results of Ouzineb et al., the objective of the current paper is to investigate and compare the use of two different static mixers (Polyacetal, PAC, from Bioblock and SMX from Sulzer Chemtech Ltd.) in the production of miniemulsions droplets. The investigation involves emulsifying mixtures of monomers with different hydrophobicities (St, MMA and butyl acrylate, BA) in an attempt to understand the role of surfactant concentration and the work done by the homogenization device in the droplet size evolution.

Experimental Part

Materials

Deionized water was used for all experiments. The monomers used were methyl methacrylate (MMA) (Aldrich, 99%), butyl acrylate (BA) (Aldrich, 99%) and styrene (St) (Aldrich, 99%). The surfactants used were sodium dodecylbenzene sulfonate (SDBS) (Acros, 88% technical grade) and sodium dodecyl sulfate (SDS) (Acros, 99%). The costabilizers used were octadecyl acrylate (ODA) (Aldrich, 97%) and *n*-hexadecane (HD) (Acros, 99%). The oil-soluble initiator 2,2′-azobis(2-methylpropionitrile) (AIBN) (Acros, 98%) was dissolved in the organic phase prior to homogenization. The water-soluble

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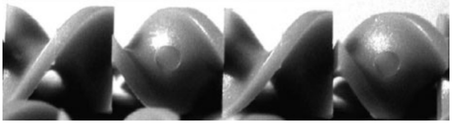

Figure 1.
Plastic polyacetal mixers from Bioblock.

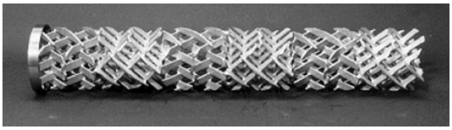

Figure 2.
SMX mixers from Sulzer (courtesy of Sulzer Chemtech).

initiator ammonium persulfate (APS) (Acros, 98%) was injected into the reactor containing the miniemulsion solution at $t = 0$. All materials were used as received.

Homogenization

The static mixers used in the initial phase of the work were made of Polyacetal (PAC) and purchased from Bioblock (France) (Figure 1).

A bundle of four elements was placed inside the tube. Each element was 15 cm in length and 0.635 cm in diameter and twisted in a helical form. In the second phase of the work, seven 8 mm SMX mixers were bound together with each element positioned 90° from the previous (Figure 2). The elements were inserted in a Teflon tube and placed in line with the pump.

The general set-up of the homogenization process consisted of the elements installed in a closed loop system with a pump, tubing, reservoir tank, and a temperature bath (Figure 3). The pump used was a positive displacement gear pump from Micropump® which had a maximum flow rate of 5.4 L/min and a maximum pressure drop of 8.7 bar.

Miniemulsions were prepared with the formulations shown in Table 1 unless otherwise stated.

Monomers and costabilizer formed one phase, while the second phase comprised the surfactant dissolved in deionized water. The two phases were combined in a reservoir and then subjected to emulsification. Samples were periodically withdrawn from the 2 L reservoir vessel placed in a temperature-control led bath to avoid overheating.

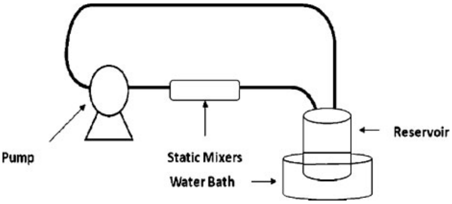

Figure 3.
Homogenization set-up for the static mixers. The set-up contained a closed loop system consisting of a pump, tubing, product reservoir and temperature bath.

Characterization

Droplet and particle size distributions obtained using the PAC static mixers were characterised using a Malvern Autosizer (Dynamic Light Scattering). The polydispersity index provided by the autosizer is based on the z-average droplet diameter (mean diameter calculated from Brownian motion); values of 0.1 and less suggest a unimodal distribution.

Complete droplet and particle size distributions reported for the SMX static mixers were measured using a

Table 1.
Formulations homogenized using the PAC and SMX static mixers.

Sample	DIW (g)	MMA (g)	BA (g)	SDS (g)	SDBS (g)	HD (g)	ODA (g)	APS (g)	AIBN (g)
SM 1	211	84.4	–	0.42	–	4.2	–	0.3	–
SM 2	211	84.4	–	0.9	–	4.2	–	0.3	–
SM 3	250	83.3	83.3	–	2.0	–	18	–	0.6
SM 4	250	83.3	83.3	–	4.2	–	18	–	0.6

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Beckman-Coulter LS-230 (Static Light Scattering). The distributions included number average (D_n) and volume average (D_v) values, the polydispersity index (PDI) was defined as D_v/D_n. Conversion for both sets of experiments was measured gravimetrically.

Polymerization

Polymerizations were carried out in a 2 L glass unbaffled, jacketed reactor equipped with a reflux condenser, nitrogen inlet, anchor stirrer, and a sampling device. All polymerizations were carried out at 70 °C. Temperature was controlled using a thermostatted bath. The impeller speed was set to 300 rpm. Initially the homogenised mixture was purged with nitrogen for ca. 25 min to remove any dissolved oxygen. Once purged, the temperature of the bath was increased from room temperature to 70 °C. The start of the reaction ($t = 0$) was defined as the moment at which the temperature in the reactor reached 70 °C. Samples were taken every 10 min for the first 30 min and then every 30 min for the rest of the experiment. Most reactions were run for three hours.

Results and Discussion

In the initial phase of the investigation we ran a series of emulsifications using the PAC static mixers and the SM 1 formulation (see Table 1). The effect of increasing the flow rate through the pump on the droplet diameter is shown in Figure 4.

Figure 4 shows the droplet diameter decreasing asymptotically with increasing homogenization time and that smaller droplets are obtained at higher flow rates. Referring back to Eq. 1, using the same formulation for all three flow rates (γ constant) and simultaneously increasing the work done by the pump (W_{breakage}), we observe a faster change in droplet area and, subsequently, larger surface areas (ΔA) and hence a smaller average droplet size. In other words, an increase in mechanical energy can help overcome the barriers imposed by interfacial tension, thereby inducing more breakage. The PDI for the final droplets at $t = 50$ min at the higher flow rates of 60.6 and 62 mL/s was 0.1; this is compared to 0.25 obtained when homogenizing at a flow rate of 36.7 mL/s. One might speculate that at higher flow rates, more energy is input into the system allowing to break up large droplets thereby narrowing the distribution and decreasing the average size. However, a deeper understanding of droplet formation and the shear stresses involved is required in order to make any further conclusions.

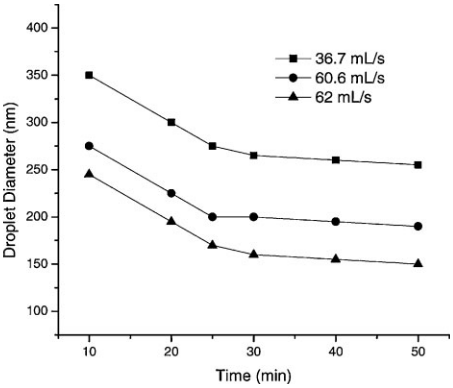

Figure 4.
Evolution of droplet size over time as a function of the flow rates (36.7, 60.6 and 62 mL/s).

The second parameter evaluated with the PAC mixers was the effect of increasing the surfactant concentration on the droplet diameter (Figure 5).

Using formulation SM 1, the surfactant concentration was varied. Formulations containing surfactant concentrations of 0.5, 1.4, 2.0, and 3.0 g/L were homogenized at a superficial rate of 60.6 mL/s. As one might expect, smaller droplets are obtained at higher surfactant concentrations. One of the primary roles that surfactant plays in a homogenization process is that it lowers the interfacial tension (γ) thereby facilitating droplet breakage. Once droplets have been created, the surfactant stabilizes the newly-formed droplets and prevents coalescence. As examined before, the trend observed in Figure 5 can be also explained using Eq. 1. Homogenizing at a constant flow rate of

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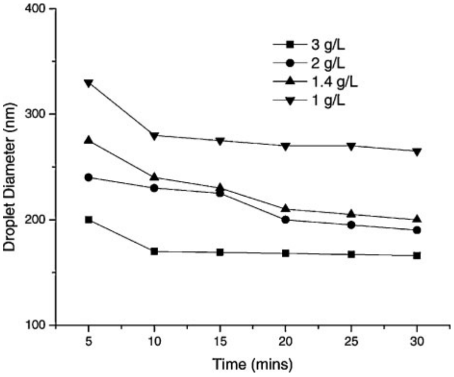

Figure 5.
Droplet diameter over the homogenization time as a function of surfactant concentration (3, 2, 1.4 and 1 g/L).

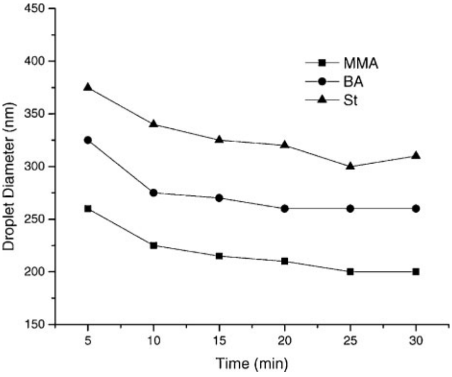

Figure 6.
Evolution of the droplet diameter over homogenization time as a function of monomer hydrophobicity.

60.6 mL/s for all emulsifications, the amount of work done on the system is assumed to remain constant (W_{breakage}). Increasing the surfactant concentrations from 1–3 g/L lowers the interfacial tension (γ) in the system resulting in an increased surface area (ΔA) and hence smaller droplets. However, it should be noted that when generating droplets one needs to look at the minimum amount of surfactant required to maintain stability and simultaneously avoid secondary nucleation due to an excessive amount of surfactant in the aqueous phase. Although 3 g/L of surfactant is desirable, its increased amount in the aqueous phase could facilitate secondary (homogeneous) nucleation.

The last parameter that was investigated using the PAC static mixers was the relationship between monomer hydrophobicity and the final droplet size. MMA in formulation SM 1 was replaced with BA and St separately (Figure 6). The water solubilities of MMA, BA and St are 150, 11 and 3.5 mol/L at 25–50 °C respectively; the measured interfacial tensions were 3.6, 7.6 and 10 mN/m.[8]

In Figure 6, it can be seen that the droplet diameter of all three monomers decreases during homogenization and reaches a plateau. The final droplet sizes differ by as much as 100 nm, with MMA being smaller than BA which in turn is smaller than St. Similar to the observations with varying surfactant concentration, MMA has a lower interfacial tension resulting in a larger surface area and hence a smaller average droplet diameter. This is compared with St, which is a much more hydrophobic monomer, and results in a smaller overall surface area and, consequently, a larger average droplet diameter. Therefore, when more hydrophobic monomers having a higher interfacial tension are used, larger droplets are expected based on a constant amount of mechanical energy. To create droplets of similar sizes to those of monomers of different hydrophobicities, one would need to investigate increasing the rate of mechanical energy input or increasing surfactant concentration, thereby lowering the interfacial tension.

The second phase of the investigation began with a comparison between the PAC and SMX static mixers. The main differences between them are their configurations and material of fabrication. The PAC mixers are helical in shape and are made of a plastic while the SMX mixers are composed of stainless steel crossbars aligned at 45° to the pipe axis. A comparison between the two static mixers based on droplet evolution using formulation SM 2 was performed (Figure 7). The miniemulsion formulations were pumped through at a flow rate of 133 ml/s.

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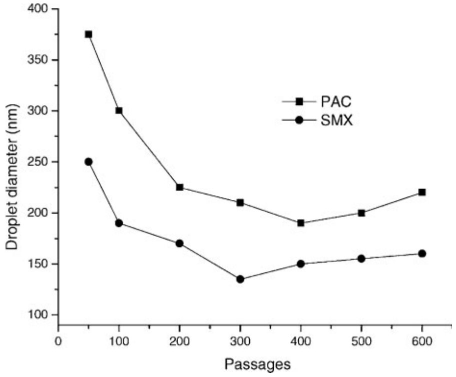

Figure 7.
Droplet evolution over time generated using the PAC and SMX mixers.

It can be seen from Figure 7 that smaller droplets were generated using the SMX mixers compared with the PAC mixers. It should be noted that the polydispersity indices (measured with a Malvern Autosizer) of the miniemulsion droplets generated using both devices were very similar (0.16 vs 0.1 for PAC and SMX, respectively). Based on these encouraging results, the next step was to emulsify an MMA/BA 50:50 wt.% miniemulsion formulation (typically used in industrial coating applications) in the SMX mixers. Miniemulsions with droplet diameters of ~110 and ~190 nm were prepared using formulations SM 3 and SM 4, respectively (Figure 8). The formulations were pumped through the SMX static mixers at a flow rate of 125 mL/s and samples were taken from the reservoir every 7.5 min (Figure 8A). Once the emulsification was complete, the miniemulsions were transferred and polymerized in a batch process (Figure 8B).

As Figure 8 (A) shows (and as observed previously), doubling the amount of surfactant in the system (while maintaining a constant flow rate of 125 mL/s), generates smaller droplets (80 nm) with a narrower PDI (1.5 vs. 2.5; by static light scattering). The formulation consisting of 2.5 wt.% SDBS produced ~110 nm droplets whereas the formulation with 1.2 wt.% SDBS produced ~190 nm droplets after 45 min. The more the mixtures pass through the static mixers, the smaller the average droplet size. However, after a certain point (30 min) it becomes increasingly difficult to further reduce the droplet size, as can be observed by a mere 10 nm drop in droplet size in the last 15 min compared to ~100 nm drop in the first 30 min.

In both cases the nonpolymerized droplet systems were found to be stable (little variation in the droplet diameter) for up to 6 h. The miniemulsion systems were polymerized in a 2-L batch reactor at 70 °C using AIBN. The evolutions of conversion and PDI are shown in Figure 8 (B). In both cases we obtained ca. 90% conversion after 2 h and maintained a fairly constant PDI. The constant PDI suggests that nearly every droplet was converted to a polymer particle. The PDI (~1.5) is smaller for the system containing 2.5 wt.% SDBS. However, even with less surfactant (SM 3) and, consequently, a wider distribution (PDI = 2.5), we managed to polymerize stable droplets as indicated by the fairly constant particle size distributions in the course of polymerization (Figure 9).

In Figure 9, we see the particle size distribution in the course of polymerizations of systems SM 3 and SM 4. There is little variance in the distributions at 90 and 180 min compared to the unpolymerized droplets at $t = 0$ minutes suggesting predominant droplet nucleation. If any particles were created through secondary nucleation, they were not stable for a time period long enough to be observed. Overall, on the basis of preliminary results obtained using the SMX static mixers, it can be concluded that smaller droplets are generated in the SMX compared to the PAC and that adjusting the surfactant concentration can lead to very good control of both droplet and particle size distributions.

Conclusion

The major focus of this work was to demonstrate the feasibility of using in

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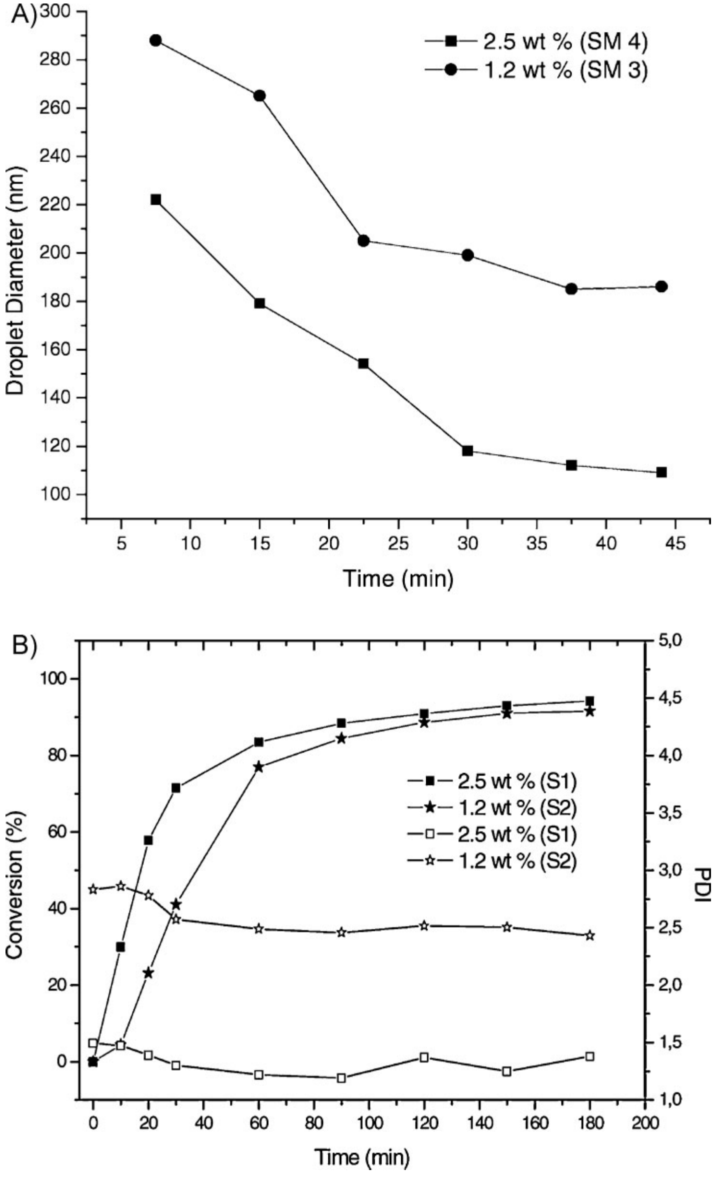

Figure 8.
A - Evolution of droplet diameter (D_v) over time as a function of the surfactant concentration. B – Evolution of conversion and PDI as a function of time for formulations SM 3 and SM 4 polymerized at 70 °C.

industry techniques generating polymerizable dispersions of droplets. Using the static mixers it was possible to generate nanosized droplets and polymerise them to obtain nearly 1:1 mapping of droplets to particles for droplets as small as 110 nm at industrially relevant solid contents of 40–60%. It was found that the average droplet size could be varied by changing the flow rate and surfactant concentration. As was expected, the droplet size decreases as both of these variables increase.

Based on the preliminary results obtained using the SMX static mixers, it can be concluded that smaller droplets are generated in the SMX compared with the

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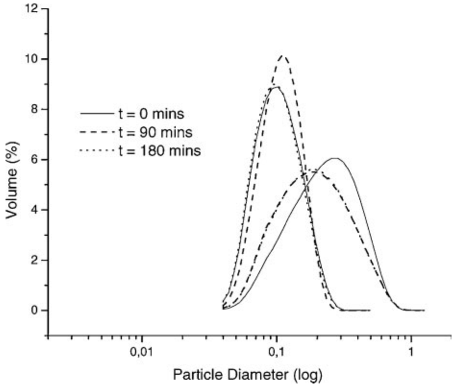

Figure 9.
Particle size distributions at 0, 90, and 180 min for the polymerised SM 3 and SM 4 formulations.

PAC and that adjusting the surfactant concentration can lead to very good control of both droplet and particle size distributions. Although these results are still preliminary, they demonstrate the potential of static mixers as miniemulsification devices. Further investigation of improving the emulsification process in terms of flow rates and formulations is required. A future paper will focus on optimization of the emulsification process by shortening the mixing time scale and developing a polymerization process in line with the emulsification step.

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