Synthesis of Polyacrylic/Silica Nanocomposite Latexes using Static Mixer

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Summary: Static mixers (Sulzer Chemtech; SMX) were used to prepare silica/ MMA-co-BA miniemulsions that were polymerized to produce nanocomposite latexes. Acceptable conditions for the formulation of polymerizable nanodroplets were found and subsequently used to produce silica/poly(MMA-co-BA) nanocomposites. The droplet size distribution of the resulting miniemulsions was narrow enough that it could be successfully polymerized. It was found that the droplet size depends on the silica content and increases with increasing the silica concentration. It was also shown that there is a relationship between the droplet size and the viscosity of the dispersed phase. The majority of droplets were nucleated upon polymerization when less than 15% silica was used. However, when the silica content exceeded 15%, the ratio of the number of particles in the final latex to the number of droplets (Np/Nd) increased to value much higher than 1 indicating the occurrence of homogeneous nucleation.

Keywords: droplet size; miniemulsion; nanocomposite; particle size; silica; static mixer

Introduction

Emulsion polymerization is widely used as a means of making a numerous commercially important products, but does not always offer the necessary flexibility in terms of particle generation needed to produce a range of composite materials. Beginning in the 1970's, researchers began to understand that if the monomer droplets were small enough, they could also capture free radicals and thus polymerize.[1] This was the beginning of miniemulsion polymerization, which has now evolved as an alternative to conventional emulsion polymerization. The ingredients of a miniemulsion system are similar to a conventional system, with the addition of a hydrophobic agent. The main difference between conventional and miniemulsion polymerization is the mechanism of particle creation.[3–5] In commercial emulsion polymerization processes, micellar nucleation is the main method of particle formation. In contrast to a conventional system, monomer droplets are much smaller (50–500 nm), and are created by some type of intensive mixing process. If they are small enough, and if there are no micelles present in the reactor they will be the main locus of polymerization. In an ideal miniemulsion, we will obtain one polymer particle per initial droplet (i.e. Np/Nd = 1). These droplets are stabilized by a two component system: the surfactant (similar to those used for conventional emulsion polymerization) and the hydrophobe.[2] The surfactant provides the steric and/or electrostatic stabilization, and the hydrophobic agent retards Ostwald ripening; that is to say the disappearance of smaller droplets that are consumed by the larger ones.

In miniemulsion polymerization, the droplets (which need to be small enough to capture free radicals at a significant rate)

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behave as individual reactors. Since they are formed by mechanical agitation, oil soluble compounds can be directly integrated into the polymer particle "ab initio" to make hybrid or composite materials (or even be used as initiators to limit water-phase reactions).

As we mentioned above, miniemulsification necessarily involves an intensive mechanical agitation step. Ultrasound (US) is traditionally used on the lab scale, but its use is limited for industrial application. For this reason, the use of more industrially efficient homogenizers such as static mixers (SMs), high pressure homogenizers or rotor-stator (RS) mixers is desirable. There are many reports concerning the use of SM for mixing two immiscible fluids, but its use for a miniemulsification process has not been well investigated and understood.

Ouzineb *et al.*[6,7] and Farzi *et al.*[8] studied the use of SM for the miniemulsification of single monomer systems like styrene (ST), butyl methacrylate (BMA) and methylmectacrylate (MMA), and showed that it is possible to make stable miniemulsion droplets in this manner. In the latter study, it was shown that it is possible to homogenize MMA with an SM assembly and to polymerize the resulting nanodroplets. It was also found that higher flow rates and well-defined mixer geometries are needed to emulsify mixtures of MMA and BA. In the current work we will build on these results, first to identify acceptable conditions for the miniemulsification of a 50/50 wt% mixture of MMA/BA. Subsequently a silica-loaded monomer was emulsified to create nanodroplets containing silica nanoparticles. These droplets were consequently polymerized using miniemulsion polymerization technique.

Experimental Details

Materials

The aqueous silica suspension used in this study was graciously supplied by Clariant (France). The main characteristics of this suspension, referred to as GEN33 are shown in Table 1. The specific surface area of silica particles was determined from nitrogen adsorption isotherms using the Brunaeur, Emmett, Teller (BET) method. The diameter of the silica particles and polydispersity index (PI) were determined by DLS using a Malvern Autosizer.

Table 1.
Characterization of supplied silica particles in water

	GEN 33
Specific surface area (Sspec, m2/g)	50.5
Particle diameter (DSiO2, nm)	78
Polydispersity index (PI)	0.020
Solid content (SC, %)	27
Suspension pH	9.57

γ-methacryloxy propyl trimethoxysilane (γ-MPS, Acros organics) was used as coupling agent through this work.

Absolute ethyl alcohol (99.8%) and methyl alcohol (99.9%) were obtained from Carlo Erba, and used as received. MMA, BA, octadecyl acrylate (ODA; the hydrophobe) and ammonium persulphate (APS; the free radical initiator) were obtained from Acros and used as received. Disponil A3065 and Disponil FES 32S are non-ionic (TN) and anionic (TA) surfactants, respectively and were graciously supplied by COGNIS France.

Miniemulsification Procedure

As mentioned before, it was shown in our previous work[8] that it is possible to create stable miniemulsion of one single monomer like MMA using a set-up of 8 mm diameter SMX static mixer shown schematically in Figure 1. The SM set-up consisted of 7 elements of 0.7 cm (these were 8 mm elements machined down to 7 mm in order to fit in the tube) placed in a polytetrafluoroethylene (PTFE) housing. This housing was attached to a longer nylon tube with the same diameter, through which the liquid phase was recycled during homogenization. A pump with a theoretical pressure loss of 8.7 bar and maximum flowrate of 133 ml/s of emulsion was used to recirculate the fluid.

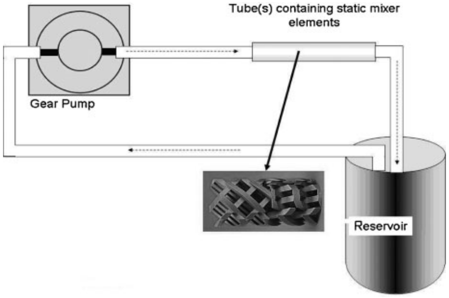

Figure 1.
Static mixer homogenisation set-up.

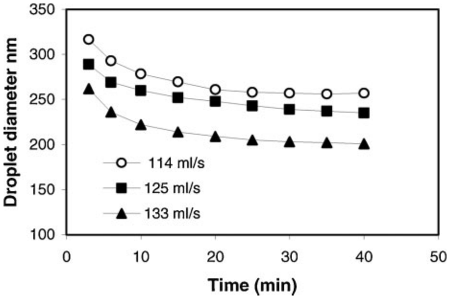

Figure 2.
Evolution of droplet diameter as a function of recycle time.

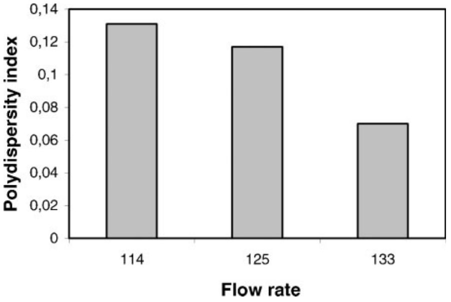

Figure 3.
Polydispersity of miniemulsions after 30 minutes homogenization.

Results and discussions

Formation of mixed monomer droplets

The objective of this initial section is to find acceptable conditions for the formation of nanodroplets and polymerization of a 50/50 MMA/BA mixture. For this purpose, the droplets need to be small enough so that they may successfully compete for free radicals and monomodal enough that they can be polymerized successfully.[1,9] The mixed monomer system (MMA/BA 50/50 wt %) was homogenized using the SMX mixing elements according to the recipe given in Table 2. The flow rate of the pump was varied from 114 ml/s to 133 ml/s and breakage of droplets was studied. Figure 2 shows the evolution of droplet diameter of miniemulsions as a function of recycle time for increasing flow rates. It can be seen from this figure that regardless of the flow rates, the droplet diameter decreases with increasing homogenization time and then reaches a plateau. As expected, Figure 2 also shows that smaller droplets are obtained at higher flow rates.

The polydispersity indices (value reported by Malvern Software. A value of less than 0.1 is considered to be monodisperse) of miniemulsions thus created is shown in Figure 3. As can be seen, the polydispersity index of the miniemulsion created at higher flow rate is the smallest.

These dispersions were polymerized via a batch process in a cylindrical glass reactor (150 ml) with a nitrogen inlet. Droplet diameters of miniemulsions after 30 minutes of homogenization, conversion of polymerization reaction after 120 minutes, particle size and polydispersity index of latexes and also N_p/N_d are given in Table 3 for different flow rates.

The highest flow rate gave the narrowest DSD and smallest average diameter. Upon polymerization, this dispersion yielded the narrowest PSD with N_p/N_d closest to unity,

Table 2.
Miniemulsion recipe

Water	Monomer	Hydrophobic agent	Surfactant (active matter)	Initiator
69.35 g	28.1 g	2 g (ODA)	0.17 g TA, 0.26 g TN	0.12 g APS

Table 3.
Effect of flow rate on characteristics of samples

Flow rate	D_d	Conversion	D_p	PI	N_p/N_d
114	257	0.95	181	0.082	2.39
125	235	0.97	183	0.076	1.76
133	201	0.96	189	0.056	1.11

indicating efficient nucleation of the nanodroplets.[10] The best condition that we obtained corresponds to the flow rate of 133 ml/s. Therefore, this condition was used in the following experiments.

Droplet Formation of Silica Loaded Monomer

Miniemulsions with different silica contents were prepared from a master batch of a relatively high concentrated dispersion of silica in monomer (35 wt % silica relative to MMA/BA 50/50 by weight), which were diluted to the desired concentration of silica by adding monomer prior to homogenization.

Stable miniemulsions were created by homogenization of silica-containing monomers in aqueous solution of surfactants using the set-up in Figure 1 and the recipes given in Table 2, and with silica concentrations varying from 0 to 20% w/w relative to total monomer. Droplet size is illustrated in Figure 4 as a function of homogenization time for different silica contents. As can be seen, droplet size decreases as a function of homogenization time as in the case of the unloaded dispersions shown in Figure 2. The results also show that droplet size increased with increasing silica content. At 20 wt % silica content droplet size is very close to that of 15 wt % silica content. This could be due to the fact that when silica content reaches 15% the viscosity of dispersed phase is relatively high and the energy dissipated by SM might not be enough to break up the droplets as much as samples other samples with lower silica content. General forms of these curves are similar to those obtained for silica-free system; however the presence of silica particles slightly changes the behaviour of system. It worth mentioning that this phenomenon has reported in literature both for silica particles[11] and titanium dioxide.[12–14] The increasing monomer droplet size containing titanium dioxide has been contributed to the lower adsorption of surfactant on the droplets in the presence of hydrophobic titanium dioxide particles.[13]

The evolution of the polydispersity index for miniemulsions as a function of silica content is plotted in Figure 5, where it can be see that this quantity increases as the silica content does. This could be due to the distribution of silica particles in the droplets. Silica particles form a circular configuration at the interface of monomer/water and create some large droplets.

Effect of the Silica Particles on Polymerization

The conversion of reaction for silica contents varying from 0 to 20% versus time is

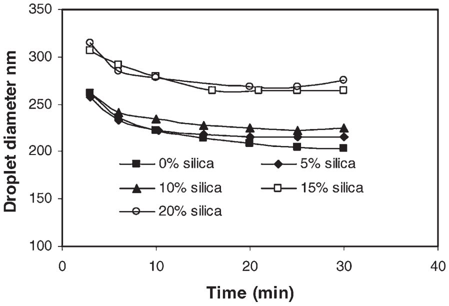

Figure 4.
Evolution of droplet diameter versus homogenization time.

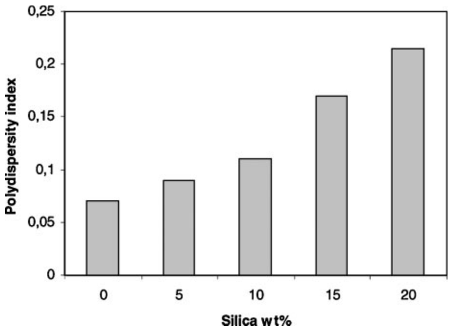

Figure 5.
Evolution of polydispersity index as a function of silica content.

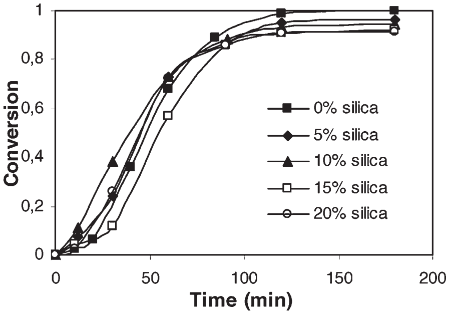

Figure 6.
Conversion of polymerization for miniemulsion with different silica content.

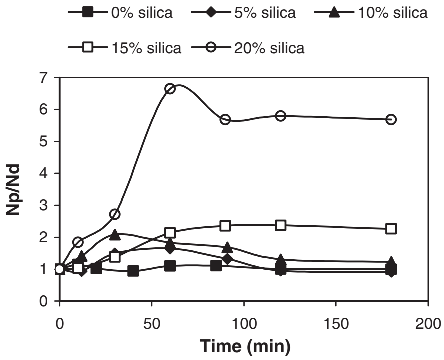

Figure 8.
Monitoring of Np/Nd during polymeization.

shown in Figure 6. There does not appear to be a clear dependency of conversion on silica content.

Figure 7 shows the evolution of particle diameter as a function of polymerization time. As can be seen from this figure, particle size decreases at the beginning of the polymerization and then slightly increases and reaches to a plateau. As stated previously this increase can be attributed to the homogeneous nucleation[15] at the beginning of reaction, followed by the coagulation of newly created particles (There might not be enough surfactant in the system to fully stabilize the renucleated particles). When the silica content is greater than, or equalt to 15 wt % the final average particle size is smaller than in cases with less than this limit. This suggests that a significant number of new particles created by secondary nucleation appear to be stabilized. This is perhaps due in part to a contribution of partially modified silica to the stabilisation of the particles. Since there is more of it, this might contribute to the stabilisation of the silica containing particles. Also since the droplet size increases as the silica content goes up, it is possible that the more silica we have in the mixture, the more free surfactant is available in the water phase, and the more it is possible to stabilize small particles created via homogeneous nucleation. In any event, creation of new particles during polymerization can be clearly seen from Figure 8 where we see the PI of miniemulsions as a function of time for different silica content. Here, the PI decreases during polymerization and at the end of polymerization it is slightly higher than 0.1 for silica content higher than 10% and lower than this value for silica content less than 10%.

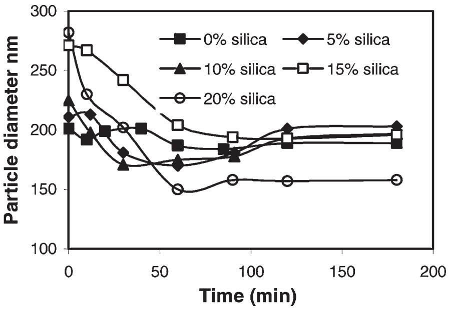

Figure 7.
Evolution of particle diameter during polymerization.

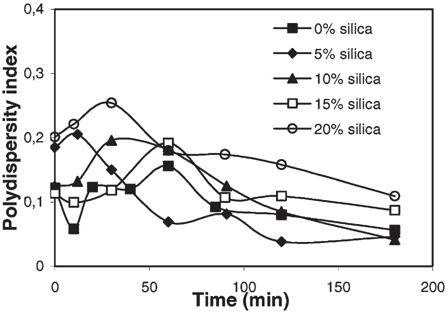

Figure 9.
Variation of polydispersity during the polymerization.

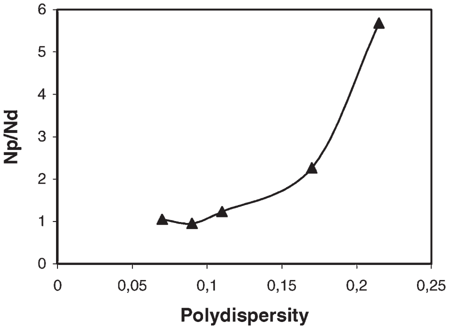

Figure 10.
Effect of the polydispersity of miniemulsion on Np/Nd.

The variation of N_p/N_d as function of PI is shown in Figure 10. It should be noted that when PI is close to 0.1 and the DSD of a miniemulsion is relatively narrow, N_p/N_d remains closer to unity during and at the end of polymerization. This suggests that PI has an important effect on the nucleation step and a good droplet nucleation can be occurred if droplet size is small enough and DSD is narrow enough.

Conclusion

A Sulzer SMX mixer set-up was successfully used as homogenization device for the miniemulsification of a mixture of monomers (MMA/BA 50/50 wt%). Then the same homogenization system was used to disperse silica-loaded monomer. The resulting miniemulsions had narrow enough DSD to be successfully polymerized to prepare silica/polyacrylate composite nanoparticles. It was found that the droplet size depends on the silica content and increases with increasing the silica concentration. It was also shown that there is a relationship between the droplet size and the viscosity of the dispersed phase. The majority of droplets were nucleated upon polymerization when less than 15% silica was used. However, when the silica content exceeded 15%, N_p/N_d increased to value much higher than 1 indicating the occurrence of homogeneous nucleation.

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