

High solids content emulsion polymerisation without intermediate seeds. Part III. Reproducibility and influence of process conditions

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Abstract

The reproducibility and robustness of a unseeded process for the production of high solid content, low viscosity latex are examined. A series of runs showed that the experiments are very reproducible both in terms of the particle size distribution and the shear viscosity of the final latex. It is also shown that it is the surfactant concentration and feed profiles that are the most sensitive issues in maintaining product specifications since they control the rate of generation of small particles.

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1. Introduction

In previous papers, Boutti et al. [1–3] developed a process for the production of high solid content, low viscosity lattices without the use of intermediate seeds. This process consists of four stages:

- Stage 1: the creation of a well-defined number of particles that will form the initial population.
- Stage 2: the concentration of this initial population of particles to approximately 60% solids.
- Stage 3: the introduction of a second population of particles into the first population.
- Stage 4: the concentration and parallel growth of the two populations.

In Part I of this series of papers [2], the authors showed that the best way to produce the first population of particles (stages 1 and 2) was to use an electrically neutral initiation system (hydrogen peroxide/ascorbic acid: HPO/AscA). A small amount of anionic surfactant was used in conjunction with a non-ionic surfactant in stage 1, and then in stage 2,

the stabilisation of the growth phase was ensured using non-ionic surfactant alone. In fact; the surfactant levels were continuously adjusted in order to maintain a surface coverage of approximately 85% (assuming no surfactant partitioning—the real values will be slightly lower). The effect of this was to maintain a relatively constant number of large particles, and create conditions, whereby the small particles flocculate onto the larger ones. Not only does this have the effect of avoiding the formation of fine particles, it also helps the larger ones to grow faster. Once a solid content of approximately 60% was reached, the redox system was consumed by heating and stopping the AscA flow. The latex was then covered by a mixture of TA and TN, and then the polymerisation was initiated with APS. Monomer, APS and TN were then added continuously for a certain time in order to gently create the second population of small particles and to concentrate the latex. It was demonstrated that using this process allowed the authors to attain solids contents of 74% (v/v) with a viscosity of 1581 mPa s at a shear rate of 20 s⁻¹. Duplicate runs were reported, suggesting that the process is reproducible, and no difficulties with floc formation or loss of stability were reported.

These results can be viewed quite positively, but it is equally important to demonstrate the reproducibility, the robustness and the influence of the different parameters such

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as flow rates and concentrations on the results. Indeed, it has previously been reported that one of the major difficulties with in situ nucleation is the lack of reproducibility of the processes and the sensitivity of the process to changes in process conditions [4]. The objective of this paper is to take the process described in Ref. [3], and to examine these different points.

2. Experimental

The monomers used in this study were methylmethacrylate (MMA), butyl acrylate (BA) and methacrylic acid, all obtained from ACROS (Isle d'Abeau, France) and used as received. The copolymers always contained 20% by weight MMA, and 78–80% by weight BA, with the difference being made up from MAA. The initiators used in the experiments were ammonium persulphate (APS), or the redox pair hydrogen peroxide/ascorbic acid (HPO/AscA). All products were obtained from ACROS (Isle, d'Abeau, France) and used as received. The anionic surfactant (TA) was Disponil® FES 32 IS (sodium salt of ethoxylated fatty acid with sulphate group groups), and the non-ionic surfactant (TN) was Disponil® A 3065 (mixture of linear ethoxylated fatty acids with alcohol end groups). Both surfactants were supplied by Cognis (France) and used as received, and the results of their characterisation were presented elsewhere [5].

The concentrated intermediate latices used here (i.e. the population of large particles) were produced as described in Part I (in fact, some of the latices described therein were used in Part II, so particular attention is paid to keeping the same nomenclature), and the experimental procedure for the complete process is detailed in Part II [2,3]. Only deviations from the general procedure described in these papers will be mentioned here. Recall that the 'first populations' are described in Part I [2], and the names of the different latices used in the current paper are the same as those in the earlier ones. The same is true of the bimodal runs in Part II [3].

3. Results and discussion

3.1. Reproducibility

Once the process is developed, one of the most important

aspects is to study its reproducibility. In this section, we will compare three experiments with almost identical conditions.

The experimental procedure for three runs that were carried out under similar conditions is shown in Table 1. E3.24 and E3.25 are identical. E3.30 does not use the same first population as the other runs, but is otherwise the same (this run was detailed in Part II). The main characteristics of the corresponding final products are summarised in Table 2.

The main characteristics of E3.24 and E3.25 are very similar, and for E3.30 we observe a slight difference that is most likely due to the fact that the first population is not the same for this run, (the average particle sizes of the first populations were $d_{pE2.327} \approx 507$ nm and $d_{pE2.328} \approx 580$ nm [2]).

The reproducibility of the process has been verified at different levels. Fig. 1 shows the final PSD determined by static light scattering (SLS) for these three runs. It is worth noting that for E3.30, the first population, E2.328, has slightly larger particle diameter and slightly higher initial surface coverage. This means that a bit more surfactant is available to stabilise new small particles. However, as can be seen in Table 2 and Fig. 1, the PSD determined by SLS is very reproducible for E3.24 and E3.25, and a small difference is observed for E3.30, where the fraction of small particles is slightly lower.

The viscosity of the raw final products, and that of the same latexes diluted to a polymer content of 70% are plotted as a function of the shear rate in Fig. 2. The reproducibility of the PSD is reflected in the viscosity curves (in order to get such similar rheological behaviour, it is necessary to have very similar PSD). Indeed, for similar polymer content similar viscosity values are observed and the shear thinning behaviour is the same for all three runs. Moreover, after dilution the viscosity decreases in the same way for the three runs. These results show the high reproducibility of the process.

The reproducibility of the reaction rate calculated from the gravimetric conversion measurements is presented in Fig. 3. As can be seen here, the evolution of the reaction rates is also very reproducible for these three runs. Given that the concentration of initiator and monomer is the same for all the runs, the reproducibility of the kinetics also proves that the PSD evolves in the same way for all the runs.

Finally, the reproducibility of the composition of the polymer was measured using differential scanning calorimetry (DSC), the results of which are shown in Fig. 4. DSC analysis were performed on polymer obtained by drying the

Table 1
Detailed experimental procedure for runs E3.24, E3.25 and E3.30

Run	First population	PC _i (%)	$\theta_{i\text{theoretical}}$ (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.24	E2.327	58	85	1.43	1.6	0.31	40
E3.25	E2.327	58	85	1.37	1.6	0.31	40
E3.30	E2.328	58	96	1.40	1.6	0.26	40

Table 2
Final characteristics of the latexes E3.24, E3.25 and E3.30

Run	PC (%)	η (mPa s) at 20 s^{-1}	η (mPa s) at 20 s^{-1} PC= 70%	Large population		Small population	
				d_p (nm)	%V	d_p (nm)	%V
E3.24	74.4	1460	343	1109	84.4	213	15.6
E3.25	74.1	1320	370	1074	82.4	244	17.6
E3.30	74.1	1581	395	1140	86	192	14

latex, and the apparatus used is the Setaram DSC 131. Fig. 4 shows that the composition of the polymer is also very reproducible. The Fox equation predicts a glass transition temperature of about -34°C according to the weight fraction of each monomer and the glass transitions temperature of the corresponding homopolymers. This value corresponds to the one measured in the first change of slope. However, a second change of slope at higher temperatures can also be seen. This change of slope was observed for all of the latexes analysed, which allows us to interpret it as a T_g with confidence. This second glass transition reveals the presence of particles richer in MMA. This observation is not unexpected since we know that an important part of the nucleation occurs according to the homogeneous nucleation mechanism in the aqueous phase that is richer in MMA than in BuA.

3.2. Influence of the surface coverage or concentration of surfactant

As discussed in Part II [3], the addition of the renucleation surfactant solution (30 wt% TA and 70 wt% TN in terms of active components) allows us to maintain a certain amount of anionic surfactant in the aqueous phase (enough to help promote the creation of particles via homogeneous nucleation). Nevertheless, an attempt is made to keep a relatively low concentration of surfactant ($\theta_{\text{theoretical}} < 100\%$) to ensure that particle creation is moderately gentle, and that we avoid a massive creation

of particles and thus surface area that could provoke a redistribution of surfactant in the reactor. For the run E3.23 the initial concentration of surfactant is increased to $\theta_{\text{theoretical}} = 100\%$, as shown in Table 3. This run is compared to E3.25, which, given its reproducibility, can be used as a ‘reference’ run. E2.23 and E3.25 are carried out in similar experimental conditions except for $\theta_{\text{theoretical}}$ that remains below 100% for the reference runs. Also, the amount of initiator with respect to the added monomer is slightly higher for E3.23.

The PSD for both experiments a short time after the beginning of the renucleation stage are shown in Fig. 5, and the final characteristics of the latexes for both experiments are presented in Table 4. The modification of the initial concentration of surfactant can be expressed as a modification of $\theta_{\text{theoretical}}$. It can be seen from Fig. 5 that the fraction of renucleated particles is higher for E3.23 ($\theta_{\text{theoretical}} = 100\%$) than for E3.25 ($\theta_{\text{theoretical}} = 85\%$), but above all, the new particles are much smaller. Since the initial amount of surfactant available in the aqueous phase is higher for E3.23, a higher surface area can be stabilised, and renucleated particles are stabilised earlier when they are still very small. For E3.25, to reach a surface area that can be stabilised by the surfactant available, renucleated particles have to continue to flocculate, which explains why we obtain larger particles.

Fig. 6 shows the PSD for E3.23 at 17 and 30 min after the beginning of the renucleation. As can be seen here that we observe the appearance of very large entities of about $100 \mu\text{m}$ about 30 min after the beginning of the renucleation stage in run E3.23. This peak corresponds to the formation of coagulum. Shortly afterward, the system is entirely destabilised and we obtain the formation of scrap as indicated in Table 4. It can therefore be concluded that the amount of surfactant initially available for the renucleation is too high in run E3.23, and that the renucleation is therefore rapid, and uncontrolled due to the development of a very large surface area. The stabilisation of these new particles leads to the redistribution of the surfactant, which destabilises the system. This observation confirms the hypothesis reported in the literature to this effect [6]. It is worth noting that the concentration of APS was slightly higher for E3.23, but this did not help to stabilise the large particles.

Fig. 7 shows the evolution of the PSD during the renucleation stage for E3.25. In this case no formation of

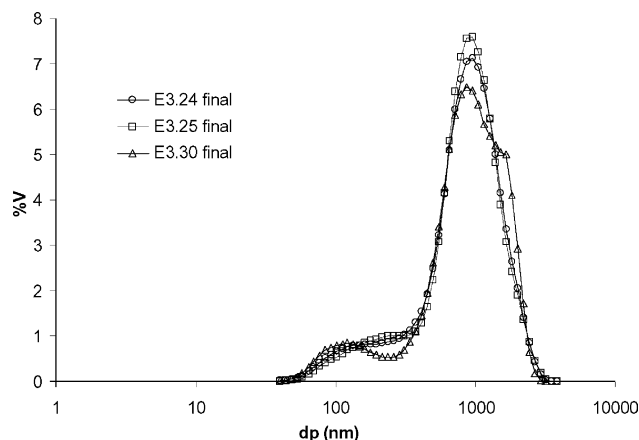


Fig. 1. Reproducibility of the PSD.

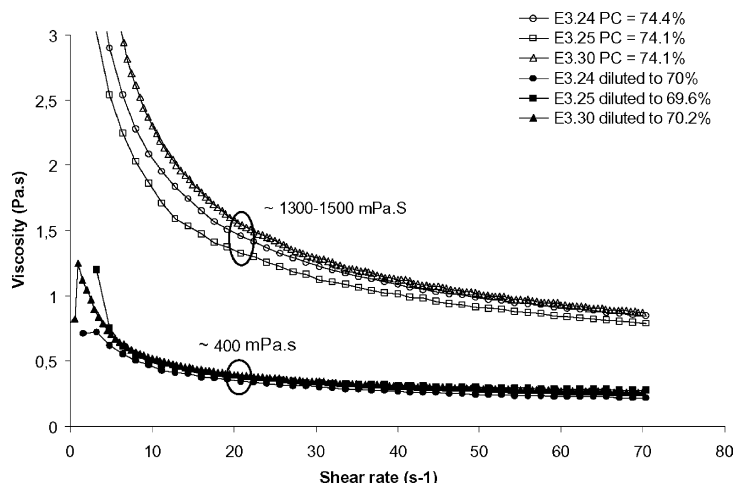


Fig. 2. Reproducibility of the viscosity.

Table 3
Detailed experimental procedure for runs E3.23 and E3.25

Run	First population	PC ₁ (%)	$\theta_{\text{theoretical}}$ (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.23	E2.327	58	100	1.15	1.6	0.45	40
E3.25	E2.327	58	85	1.37	1.6	0.31	40

Table 4
Final characteristics of the latexes for the runs E3.23 and E3.25

Run	PC (%)	Large population		Small population	
		d_p (nm)	%V	d_p (nm)	%V
E3.23	Coagulum	–	–	–	–
E3.25	74.1	1074	82.4	244	17.6

coagulum is observed. Small particles are continuously nucleated, and either continue to grow while new small particles appear, or flocculate onto existing particles. This can be seen in Fig. 7, where the small particles present at 90 min are no longer apparent at 120 min. However, at the end of the synthesis, new small particles have been nucleated and the fraction of small particles is high enough to have a significant impact on the viscosity. Indeed, the

viscosity of the final latex is 1320 mPa s at 20 s^{-1} for a polymer content of 74%. In this case the renucleation has been controlled since the fraction of small particles does not increase sharply, and the colloidal stability of the system is preserved despite a lower concentration of APS and surfactant for this run than for E3.23.

For each sample withdrawn during the polymerisation, the PSD is determined by SLS. From the average volume

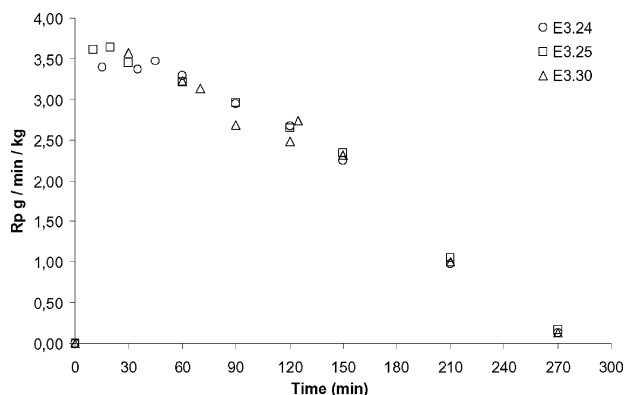


Fig. 3. Reproducibility of the kinetics.

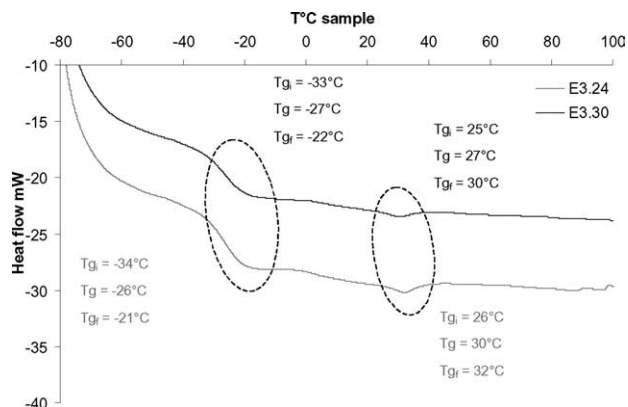


Fig. 4. Reproducibility of the composition of the polymer.

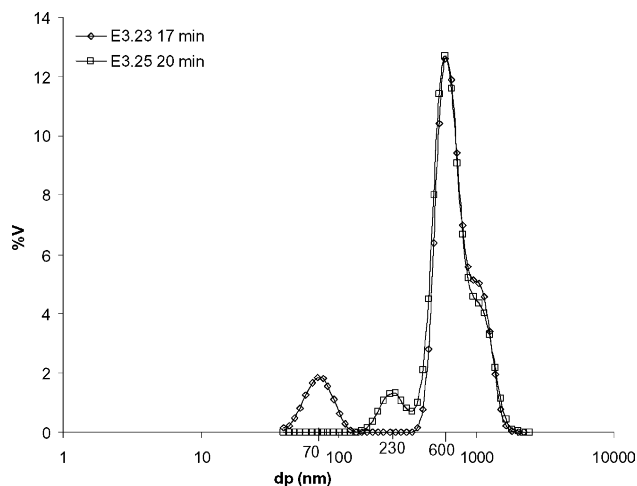


Fig. 5. Influence of the initial surface coverage on the renucleated population a short time after the beginning of the renucleation.

fraction and particle diameter provided for each population, we recalculate the surface coverage. This way of calculation allows us to take both populations into account separately in order to calculate a surface coverage as close to what we could find in the reactor as possible. The surface coverage calculated in this manner is plotted as a function of the reaction time for the run E3.25 in Fig. 8. Once again, this surface coverage is calculated assuming that all the surfactant is on the particle surface (therefore θ calculated this way overestimates surface coverage, and underestimates the quantity of surfactant in the water).

During the last hour the flow rate of non-ionic surfactant was increased in order to provide an additional stabilisation to the latex, this is what we called ‘over stabilisation’. Even if we know that the calculation of θ in this manner is not exact, it is interesting to note that it oscillates around the value of 100% during the critical stage of the process. First, this confirms that it is not necessary to be above 100% of surface coverage to nucleate new particles with the system studied. In our system we observe formation of new particles for surface coverage higher than 100%, but also

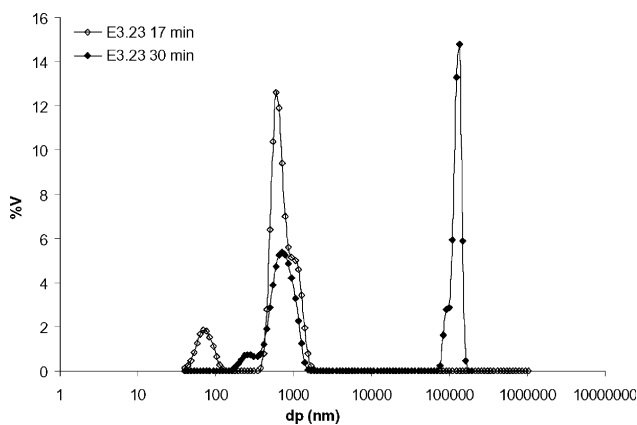


Fig. 6. Influence of the initial surface coverage on the PSD during the renucleation stage.

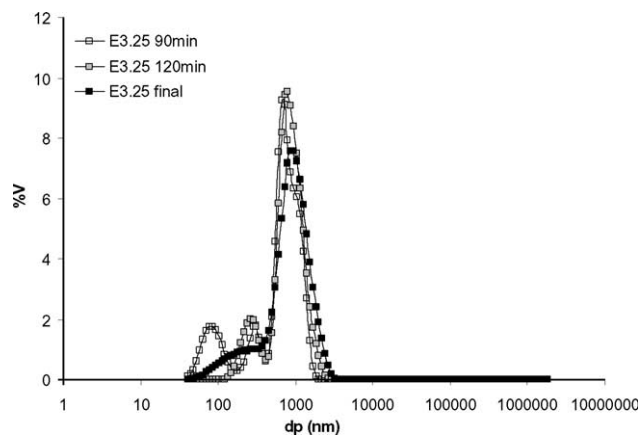


Fig. 7. Evolution of the PSD during the renucleation stage for run E3.25.

in a range of 70–80%. This is in agreement with the observation made earlier, and by Chu et al. [7,8]. These last authors found that nucleation occurred when the surface coverage of their seed latex was greater than 70%. In addition, this kind of evolution of θ shows that, even during this stage, the system oscillates between nucleation and limited flocculation. This underlines the importance of the additional non-ionic surfactant to stabilise the new particles. Moreover, the significant growth of the first population is explained by the occurrence of limited flocculation. The same observation was made by Sajjadi and Brooks [10], who proposed that the formation of new particles during the unseeded semibatch polymerisation of BuA is accompanied by the coagulation of mature particles with themselves.

Finally, as expected, the initial surfactant concentration represented by $\theta_{\text{theoretical}}$, has a significant influence on the renucleation stage. We saw that a part of TA remains in water, so when $\theta_{\text{theoretical}}$ increases, the concentration of surfactant in the aqueous phase increases. As we explained earlier we should be in the presence of mixed micelles in the aqueous phase. That is why the nucleation of new particles probably occurs by both micellar and homogeneous mechanisms. Thus, when we increase the initial concentration of surfactant, the number of mixed micelles is higher and the fraction of small particles increases sharply at the onset of nucleation, which can lead to the destabilisation of the entire system. On the other hand, when the concentration is moderate the nucleation proceeds slowly, which allows us to preserve the stability of the latex and to stabilise enough small particles to observe a significant positive effect on the viscosity.

3.3. Influence of the wt% of anionic surfactant and acid contents

In this section the weight percent of anionic surfactant in the stabilising system at the beginning of the renucleation stage on the final PSD is varied. The global $\theta_{\text{theoretical}}$ is kept in the same range of values. In these runs the monomer mixture also contains 2 wt% of methacrylic acid. Table 5

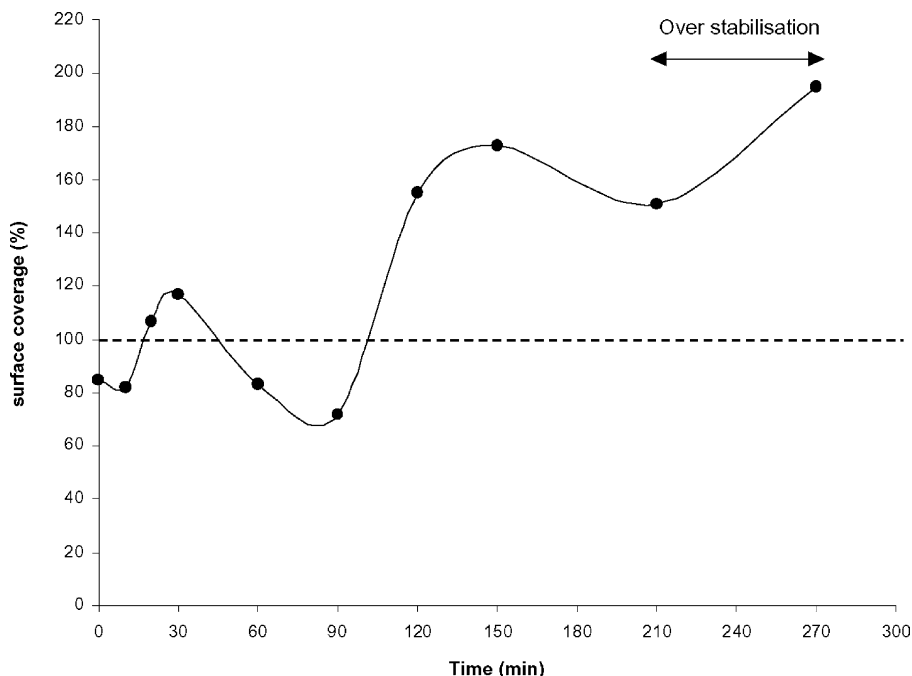


Fig. 8. Evolution of the surface coverage during the renucleation stage for run E3.25.

details the experimental procedure for each run, and Table 6 exposes the final characteristics of the corresponding latexes.

The experimental procedures are similar for all the runs except the weight fraction of anionic surfactant at the beginning of the renucleation stage. For E3.27 the amount of TA is significantly higher than for the two other experiments. There was a total break down of latex stability in experiments E3.27, where the highest TA level quickly led to the formation of scrap. Thus, it is most probably due to the fact that the high fraction of anionic surfactant involved a sharp renucleation, which destabilised the system.

Fig. 9 shows the final PSD for runs E3.26 and E3.28 determined by SLS. No scrap formation was observed for either run. The fraction of anionic surfactant is 50% higher in E3.28 (2.1 wt%) than in E3.26 (1.4 wt%), however, we do not observe a significant effect of this increase in the weight fraction of TA on the final PSD. It is likely that the difference between the two weight fractions of TA in these experiments is too small to allow us to differentiate between them on this basis. Given that 5 wt% led to the flocculation of the system, it might have been interesting to check the impact of an

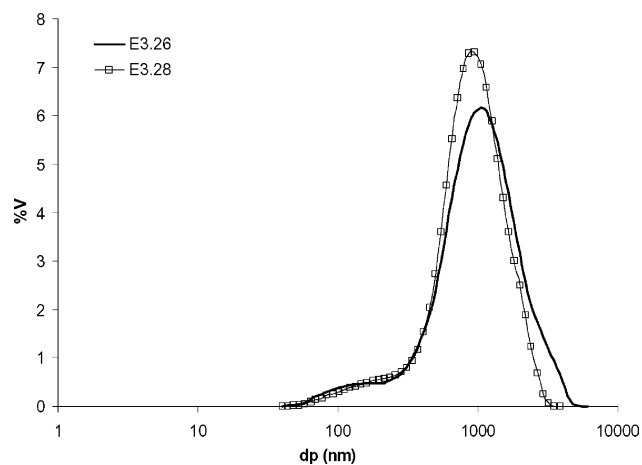


Fig. 9. Influence of the weight fraction of TA on the final PSD.

intermediate value (3 wt%) on the PSD. It is worth noting that these runs were carried out with 2 wt% of methacrylic acid in the monomer mixture. Given the high water solubility of this monomer the fraction of water-soluble species might be noticeably higher for these runs than for previous ones. These soluble oligomers carry at least one charge on their extremity since the initiation is

Table 5
Detailed experimental procedure for runs E3.26 to E3.28

Run	First population	PC ₁ (%)	$\theta_{\text{theoretical}}$ (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.26	E2.329	58	95	1.41	1.6	0.30	41
E3.27	E2.329	58	98	5.08	1.6	0.40	40
E3.28	E2.329	58	93	2.10	1.6	0.31	40

Table 6
Final characteristics of the latexes for the runs E3.26 to E3.28

Run	PC (%)	Large population		Small population	
		d_p (nm)	%V	d_p (nm)	%V
E3.26	74.3	1350	89.8	230	10.2
E3.27	Coagulum	–	–	–	–
E3.28	73.5	1129	90.1	238	9.9

done by APS but the carboxylic function is not under its ionic form since the pH of the latex ($\text{pH} \approx 2\text{--}3$) is lower than the MAA $\text{p}K_a$ ($\text{p}K_a \approx 4.5$). These molecules can provide colloidal stability and thus have an influence on the renucleation phenomenon. This aspect will be discussed in more detail below.

3.4. Influence of the surfactant solution flow rate and composition

In the process proposed here, different reagents are added after the addition of the renucleation surfactant. In particular, a solution of non-ionic surfactant is continuously added in order to stabilise the renucleated particles, but also to maintain a sufficient level of available surfactant in the aqueous phase to promote the nucleation of new particles in conjunction with the anionic surfactant. In this section we will look at the influence of the flow rate of the additional surfactant solution, as well as of the composition of this solution. Indeed, as can be seen in Table 7, for runs E3.19 and E3.20 the experimental procedure is similar for both experiments except for the flow rate of the non-ionic surfactant solution. Also, the amount of added APS with respect to the amount of added monomer is higher for E3.19.

For runs E3.29 and E3.30 the parameter studied was the composition of the surfactant solution. Actually, E3.30 is a 'typical' experiment, a mixed surfactant solution was added at the beginning of the renucleation stage, and then a solution of non-ionic surfactant was added continuously. For E3.29 the procedure is different. No renucleation surfactant solution was added before beginning to add the other components, but rather a solution of mixed surfactant is continuously added throughout the renucleation step. This solution contains water and a mixture of surfactants in the ratio of 10 wt% of anionic emulsifier and 90 wt% of TN. The total flow rates of these surfactant solutions are

the same as in experiments E3.20, E3.29 and E3.30, but the flow rate of TN in E3.29 is slightly lower than for the other runs since the solution contains TA. The flow rate of each surfactant is reported in Table 7 for each experiment. Table 8 reports the final characteristics of the corresponding latexes.

As can be seen in Table 8, the flow rate and the composition of the surfactant solution have a significant influence on the final PSD of the latexes. The final PSD of latexes E3.19 and E3.20 determined by SLS are presented in Fig. 10, and the final PSD for runs E3.29 and E3.30 are shown in Fig. 11.

For E3.20 the flow rate of TN was twice that in E3.19. This explains why the final polymer content is lower for E3.20 because if we add the same solution of surfactant twice as fast for the same period, we will of course add more water. Also, more surfactant was available in run E3.20, which implies that a higher surface area could be stabilised than in E3.19. Thus, even if the system oscillates between nucleation and limited flocculation, as we showed previously, the fraction of small particles that can be finally stabilised is higher for E3.20 than for E3.19, as can be seen in Table 8 and Fig. 10. Furthermore, since the colloidal stability is better for E3.20, limited flocculation phenomenon is less important. This might explain why a third population can be discerned at 300 nm for E3.20, whereas particles of this size mixed in with the large population for E3.19. It would be interesting to carry out another experiment similar to E3.20 (PC=70.7%) but continue for a longer time in order to reach the same polymer content as E3.19 (PC=72.5%). This would help us to understand whether or not the polymer content interacts with the flow rate of surfactant in determining the final PSD. It should also be recalled that there was more APS in E3.19 than in E3.20, but the additional stabilisation such provided is not sufficient to compensate the concentration of TN.

Table 7
Detailed experimental procedure for runs E3.19 and E3.20 and E3.29 and E3.30

Run	First population	PC _i (%)	$\theta_{\text{theoretical}}$ (%)	wt% TA	Flow rate of TN (g/h)	Flow rate of TA (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.19	E2.323	63	80	1.11	0.8	–	0.84	20
E3.20	E2.323	63	80	1.14	1.5	–	0.44	20
E3.29	E2.328	59	91	0.07	1.4	0.2	0.33	40
E3.30	E2.328	58	96	1.40	1.6	–	0.26	40

Table 8

Effect of the flow rate and the composition of surfactant solutions on the final characteristics of the latexes E3.19, E3.20, E3.29 and E3.30

Run	PC (%)	Large population		Small population	
		d_p (nm)	%V	d_p (nm)	%V
E3.19	72.5	942	80	198	20
E3.20	70.7	952	71	155	29 ^a
E3.29	73.6	1361	82.2	182	17.8
E3.30	74.1	1140	86	192	14

^a NB: small population is bimodal cf. Fig. 10.

In run E3.29, the surfactant solution contains 10 wt% of anionic surfactant, whereas in run E3.30, it contains only non-ionic emulsifier. This would explain the slight differences in the results shown in Fig. 11. Indeed, the final fraction of small particles is higher for E3.29 than for E3.30. Moreover, the size and shape of the large population peak provide some supplementary information on the development of the final PSD. The average particle size of the large population is greater for E3.29 than for E3.30 (1360 and 1140 nm respectively), and the peak is wider for the same experiment. This signifies that limited flocculation was more important for E3.29 than for E3.30. Given that the fraction of small particles is still higher for E3.29, we can conclude that more particles were created during the run E3.29 than during E3.30. However, to preserve the colloidal stability a part of the newly created particles flocculated on the particles already present to reduce the global particle surface area.

At the end of the experiment the overall amount of surfactant is similar for both runs. It is 3.12 wt%, with respect to the amount of polymer, for E3.29 and 3.27 wt% for E3.30. On the other hand, it is worth noting that anionic surfactant corresponds to 0.34 wt% of the total mass of the stabilisation system for E3.30, while it represents 7.23 wt% for E3.29. Depending on the final application of the latex it can be important to minimise the amount of ionic species in the medium.

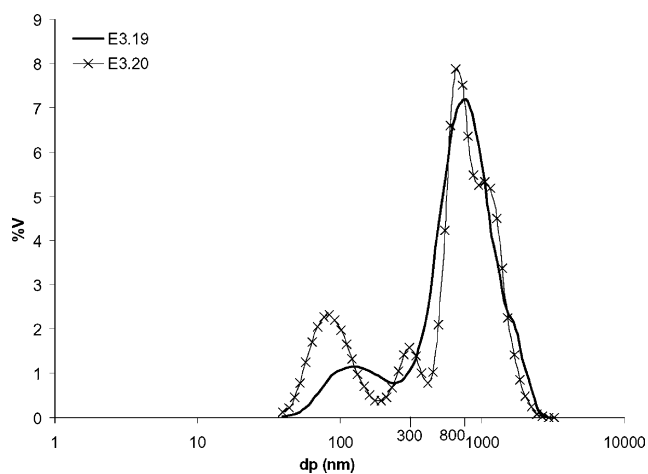


Fig. 10. Impact of the flow rate of the non-ionic surfactant solution on the final PSD.

3.5. Influence of the initiator

As explained above, APS is used as the initiator for the renucleation stage because of the stabilisation provided by the charged radicals. In this part of the study we attempted to determine the impact of the concentration of initiator on the final PSD. Table 9 details the experimental procedure for runs E3.15 and E3.17. They are both ‘complete processes’ in the sense that the first populations were not prepared ahead of time and stored for later use. The main differences between these two experiments are that the first populations of particles are not identical, and the concentration of APS is three times higher for E3.17 than for E3.15. Table 10 summarises the final characteristics of the latexes, and Fig. 12 shows the final PSD determined by SLS for both runs.

The concentration of APS appears to have a noticeable influence on the final PSD. Indeed, we obtain a higher fraction of smaller particles for E3.17 than for E3.15, and as can be seen in Table 10 and Fig. 12, the small particles are much smaller and more numerous. This means that we were able to better stabilise the newly created surface area in E3.17 than in E3.15, even though the amount of added surfactant is the same in both runs. Indeed, the final fraction of surfactant with respect to the amount of polymer is 2.83 wt% for E3.15 and 2.87 wt% for E3.17. These results show the importance of the stabilisation offered by the charges provided by APS when the other parameters are

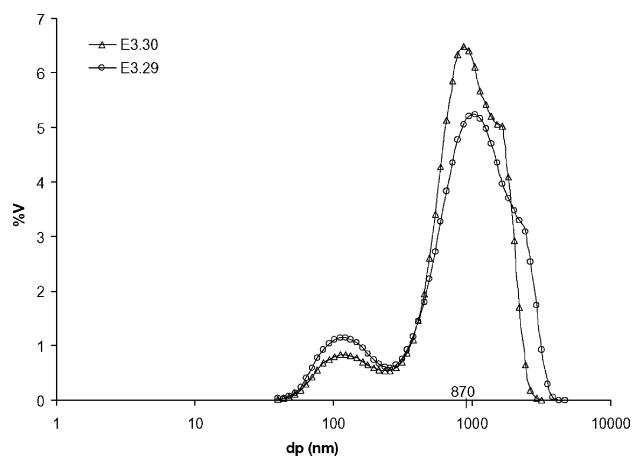


Fig. 11. Impact of the composition of the surfactant solution on the final PSD.

Table 9
Detailed experimental procedure for runs E3.15 and E3.17

Run	First population	PC _i (%)	θ _i (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.15 (CP)	E2.318	59.4	82	1.28	0.8	0.16	20
E3.17 (CP)	E2.321	61	87	1.31	0.8	0.45	20

Table 10
Effect of the concentration of APS on the final characteristics of the latexes

Run	PC (%)	Large population		Small population	
		d _p (nm)	%V	d _p (nm)	%V
E3.15	72	1110	88	244	12
E3.17	72.3	1058	82.5	144	17.5 ^a

^a NB: bimodal cf. Fig. 12.

kept constant. The same trend has been reported by Sajjadi and Brooks [10] for the unseeded semibatch polymerisation of BuA initiated by KPS. Furthermore, it confirms the importance of the nature of the initiator on the colloidal stability. Why the latex is trimodal is not entirely clear. It is possible that some of the small particles began to partially flocculate. In fact this is likely since they are too big to have simply been 'grown' from particles with $d_p = 80$ nm.

3.6. Influence of the flow rate of monomer

Another parameter that can have a significant influence on the PSD is the flow rate of monomer. Table 11 details the experimental procedure for runs E3.21 and E3.22. These experiments are carried out in a similar way except for the flow rate of monomer and the concentration of APS. For E3.22 the flow rate of monomer is twice as high as in E3.21, while the concentration of initiator is twice as low. Table 12 summarises the final characteristics of the corresponding latexes and Fig. 13 presents the final PSD determined by SLS.

Since the flow rate of monomer is lower for E3.21 and

the runs have the same total polymerisation time, the final polymer content is much lower than for E3.22. Also, the concentration of initiator with respect to the amount of added monomer is higher in E3.21, so the stabilisation provided by the charged radicals is more important for E3.21.

Despite this, we obtain a much higher fraction of small particles for E3.22, as can be seen in Table 12 and Fig. 13. Unfortunately, we cannot draw any accurate conclusions on the impact of the flow rate of monomer since the experimental conditions of the two runs are too different. It would be interesting to carry out an experiment in similar conditions as for E3.21 (PC = 65%) but with an increased final polymer content until the same value of E3.22 (70%).

Also, the concentration of initiator would have to be kept in the same range for both experiments in order to check accurately the influence of the flow rate of monomer. However, the trend discerned here, is that a higher flow rate of monomer can lead to a higher fraction of small particles. This observation is logical. Indeed, if the stabilisation provided by the surfactant and the charged radicals is sufficient to stabilise the developed surface area, the higher is the amount of added monomer, the higher is the fraction

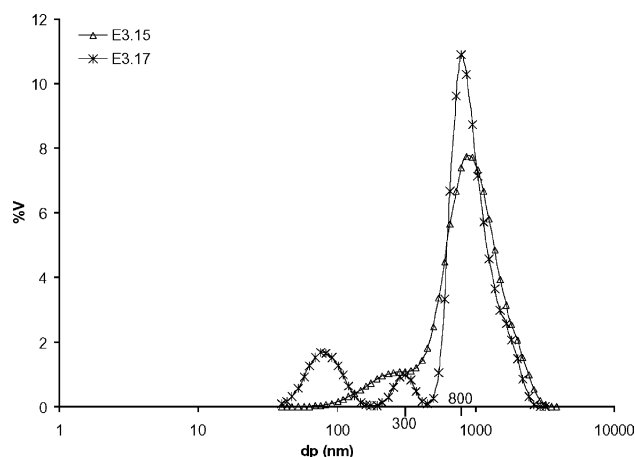


Fig. 12. Effect of the initiator concentration of the final PSD.

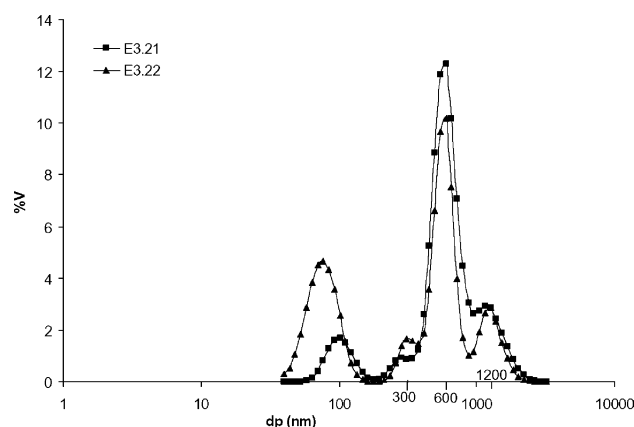


Fig. 13. Influence of the flow rate of monomer on the final PSD.

Table 11
Detailed experimental procedure for runs E3.21 and E3.22

Run	First population	PC _i (%)	θ _i (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.21	E2.324	60	84	1.14	2.7	0.95	18
E3.22	E2.324	60	84	1.15	2.8	0.53	39

of renucleated particles since the nucleation in the aqueous phase is favoured. Moreover, a higher flow rate of monomer increases the fraction of MMA in the aqueous phase, which favours the formation of water-soluble species. The increase in the concentration of these water-soluble species in the aqueous phase favours the nucleation of new particles as explained in by Tauer and Kuhn [9]. This observation is also in agreement with the results reported in the literature. Indeed, Sajjadi and Brooks [10] observed the same results for the unseeded semi-batch polymerisation of BuA, as well as Schneider et al. [6] for the copolymerisation of BuA, MMA and acrylic acid.

3.7. Influence of the presence of methacrylic acid

As we said in the introduction the composition of the mixture of monomers used in this study was chosen because of its application as a model pressure sensitive adhesive. However, in most of the industrial formulations an additional amount of acrylic or methacrylic acid is added in order to improve the mechanical resistance of the final product. At the beginning, and for the main part of this study, we chose to work only with MMA and BuA in order to reduce the complexity of the system. Now, we verify the feasibility of the process in presence the of 2 wt% of methacrylic acid in the mixture. Table 13 details the experimental procedure for runs E3.26 and E3.30. The difference between these two experiments is the composition of the mixture of monomers, and the first population, which is not identical for the two runs (although they are similar). E3.30 is a 'typical' run composed of 80 wt% of BuA and 20 wt% of MMA. For E3.26 the mixture of monomers added during the growth of the first population and during the renucleation stage is composed of 78 wt% of BuA, 20 wt% of MMA and 2 wt% of methacrylic acid. Table 14 summarises the final characteristics of the corresponding latexes, and Fig. 14 shows the final PSD determined by SLS for each run.

As mentioned previously methacrylic acid is a highly water-soluble monomer, and the fraction of water-soluble species created in presence of this monomer is higher than

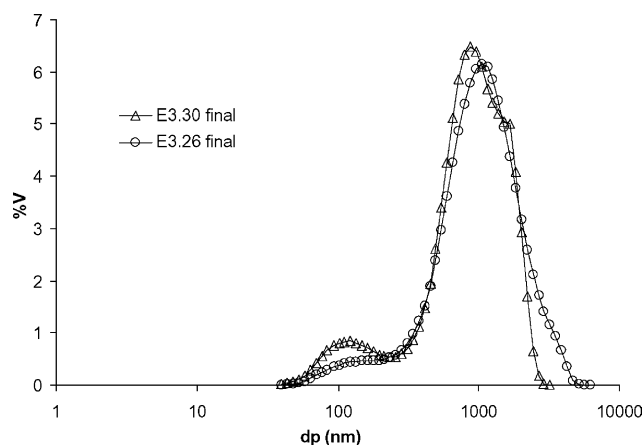


Fig. 14. Effect of the presence of methacrylic acid on the final PSD.

for the other runs. The water-soluble species formed during the renucleation stage initiated by APS are electrically charged oligomers. Thus, they can play the role of electrosteric surfactants. Moreover, a higher concentration of oligomers in the aqueous phase favours the formation of new particles [9]. That is why we would expect that the presence of MAA (methacrylic acid) might lead to a higher fraction of small particles. However, as can be seen in Table 14 and Fig. 14, the fraction of small particles obtained for E3.26 is slightly lower than for E3.30, the small particles are a bit larger and the small particle tail on the PSD is less well-defined. Also, the large population is composed of particles that are slightly larger for E3.26 than for E3.30. Even though the first population is not identical for these experiments, these results reflect a limited flocculation phenomenon that is more important in the case of E3.26, which means that the system was slightly more under-stabilised than for E3.30. The following hypothesis could explain this phenomenon. The supplementary stabilisation provided by the charged oligomers promotes significant renucleation at the beginning of step 3. However, the surface area developed quickly by these numerous small particles is very high, so, in order to maintain colloidal stability, the system is forced to reduce the global particle

Table 12
Final characteristics of the latexes E3.21 and E3.22

Run	PC (%)	Large population		Small population	
		d _p (nm)	%V	d _p (nm)	%V
E3.21	65	795	84.4	185	15.6
E3.22	70	789	60.2	126	39.8

Table 13
Detailed experimental procedure for runs E3.26 and E3.30

Run	First population	PC _i (%)	$\theta_{\text{theoretical}}$ (%)	wt% TA	Flow rate of TN (g/h)	APS (g)	Flow rate of monomer (g/h)
E3.26	E2.329	58	95	1.41	1.6	0.30	41
E3.30	E2.328	58	96	1.40	1.6	0.26	40

surface area. Thus, an important part of these renucleated particles flocculate onto each other or on particles already present. That is why small and large particles are slightly larger in the presence of MAA than for E3.30. However, it should be noted that the differences are not significant, and one could expect that the PSD could be ‘fine-tuned’ by adjusting the flow of TA/TN to get exactly the same PSD. In other words, the presence of MAA does not have a profound impact on the final PSD of the latex.

3.8. Influence of the PSD on latex viscosity

A comparison of the PSD and viscosity results for all of the runs reported here is given in Table 15, and the viscosity of each latex diluted to 70% (at a fixed shear rate of 20 s^{-1}) is shown in Fig. 15. Overall these results confirm what has been discussed in the literature [4,6]. First of all, the fraction of small particles has a strong influence on the viscosity, with the lowest viscosities being obtained when the small particles represent about 20% (v/v) of the polymer phase. The diameters of the different populations are also important. For instance, E3.18 and E3.19 both contain 80% (v/v) of large particles, but E3.18 is slightly less viscous than E3.19. This difference can be attributed to the size of the particles. Indeed, for E3.19 the larger particles are slightly smaller than for E3.18, and so the particle surface area is higher. This favours particle interactions, which makes the viscosity higher. We can also compare E3.26 and E3.28. In this case, the PSD is composed of about 10 V% of small particles for each latex, but the viscosity is lower for E3.26 because the ratio of large to small particle diameters is closer to the optimum range of 7–8.

4. Conclusion

The reproducibility of the process developed in Part II [3] has been demonstrated in terms of the PSD, rheological properties and reaction rate. It has also been verified that the process is also reproducible in presence

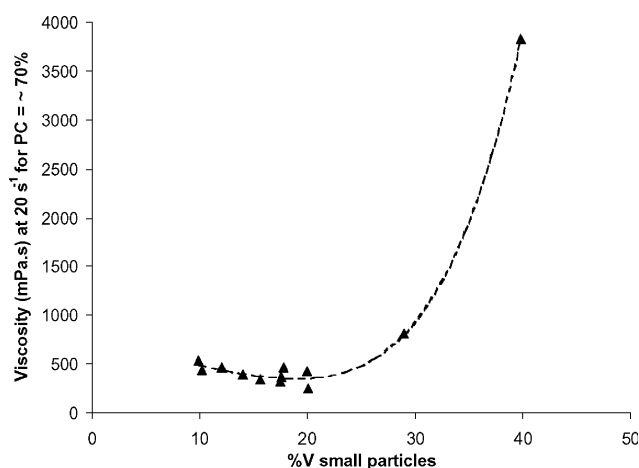


Fig. 15. Experimental viscosity values plotted as a function of the volume fraction of small particles. NB: the dashed line is simply a mean to highlight trends in the data.

of methacrylic acid in order to be close to the industrial formulations. It seems that the presence of 2 wt% methacrylic acid provokes a slight decrease in the fraction of small particles created during the renucleation step. However, the difference between the PSD with and without MAA is relatively insignificant, and it is quite likely that it would be possible to readjust the formulation to obtain the desired PSD. For instance, if the comparison was made with a latex synthesised from different initial populations, it seems reasonable to propose that an increase in the flow rate of TN during the renucleation stage in the presence of MAA would preserve a higher amount of small particles.

In so far as the effect of the monomer flow rate on the PSD is concerned, a trend has been discerned according to which the fraction of small particles increases with an increase in the flow rate of monomer. However, new experiments are needed to allow us to draw more accurate conclusions on this point.

It was also shown that the initial concentration of surfactant (or initial surface coverage) and the initial

Table 14
Final characteristics of the latexes E3.26 and E3.30

Run	PC (%)	Large population		Small population	
		d_p (nm)	%V	d_p (nm)	%V
E3.26	74.3	1350	89.8	230	10.2
E3.30	74.1	1140	86	192	14

Table 15
PSD and the corresponding viscosity for different runs

Run	PC (%)	η (mPa s) at 20 s^{-1}	Large population		Small population		η (mPa s) at 20 s^{-1} PC = ~ 70%
			d_p (nm)	%V	d_p (nm)	%V	
E3.18	71.9	984	1058	79.9	216	20.1	250
E3.17	72.3	1560	1058	82.5	144	17.5	320
E3.24	73.4	1717	1109	84.4	213	15.6	343
E3.25	72.5	2590	1074	82.4	244	17.6	370
E3.30	70.7	809	1140	86	192	14	395
E3.19	65.1	1480	942	80	198	20	430
E3.26	69.8	3835	1350	89.8	230	10.2	440
E3.29	Coagulum	–	1361	82.2	182	17.8	470
E3.15	74.4	1460	1110	88	244	12	470
E3.28	74.1	1320	1129	90.1	238	9.9	540
E3.20	74.3	1367	952	71	155	29	809
E3.22	Coagulum	–	789	60.2	126	39.8	3835

fraction of anionic surfactant are sensitive parameters that have to be well adjusted. Indeed, a high initial concentration of surfactant, especially TA, involves a strong and uncontrolled renucleation more often than not, this sharp increase in particle surface area provokes a destabilisation of the system and leads to the formation of scrap.

Finally, it appeared that the fraction of small particles could be controlled by the flow rate of added surfactant and the concentration of APS. These two reagents added continuously, provide a 'regular' stabilisation that does not involve a violent renucleation susceptible to destabilise the entire system. Actually, since they are added constantly their concentration at each moment is not high enough to provoke a strong renucleation but it is sufficient to stabilise the renucleated particles.

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