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New Routes to High Solid Content Latexes: A Process for In Situ Particle Nucleation and Growth

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Summary: A means of generating latices with solid contents well over 70% (v/v) without the use of intermediate seeds is proposed. It is demonstrated that the use of an electrically neutral initiation system (hydrogen peroxide) in the initial stages of the process, followed by an initiator yielding negatively charged free radicals (ammonium persulphate) changes the way in which the system generates stable particles. The reason for this change is the need to avoid stabilising small, homogeneously nucleated particles during the first portion of the process, and the desire to generate controlled quantities of them during the second portion. The processes are highly reproducible, as are the particle size distributions and rheological properties of the final latices.

Keywords: emulsion polymerization; high solid content; latex, viscosity; process

Introduction

For many reasons high solid content latexes (in the current content with solid contents above 65% polymer per unit volume) are attracting more and more attention. Rapid drying times, better surface coverage and reduced transportation and storage costs are just some of the reasons for this. It should be noted that solid contents on the order of 65-75% (v/v) are not considered to be "high" when we are talking about products such as caulks or sealants since the viscosity of these products is purposefully very high. On the other hand, when the products in which we are interested are paints or adhesives and must be applied in thin films very quickly, we must achieve the double objective of increasing the solid content while maintaining relatively low viscosity. As will be seen below, this requires strict control over the particle size distribution.

The limit of 65% volume fraction (henceforth solid content and polymer content will be reported in volume % unless otherwise noted) might seem arbitrary, but can be explained by a combination of theory and the results shown in Figure 1. First of all, it is well-known that randomly packed identical spheres will occupy about 64% of the volume of an infinitely large

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container. In addition, latices are obviously more complex systems than a simple ensemble of perfectly uniform spheres, and one must also include the effect of the stabilisation system in this type of analysis. Let us take the example of a perfectly monodisperse latex, stabilised by a purely anionic surfactant (e.g. SDS). One can calculate the thickness of the electronic double-layer from Equation 1:

$$\delta=\sqrt{\frac{\varepsilon k_B T}{8\pi e^2 N_A I}} \qquad \text{Equation 1}$$

where ε is the dielectric constant of water (continuous medium), k_B the Boltzman constant, T the absolute temperature, I the ionic strength, e the charge of a single electron, and N_A is Avagadro's number. The thickness of the layer is independent of the particle size, and will therefore have a relatively larger impact when the particles are small. In practice the ionic strength of our latexes will vary between 10^{-3} - 10^{-2} mol.l^{-1}. When two times the thickness of the double layer is equal to the distance between two particles, the particles come into contact. As can be seen from Figure 1, small particles will come into contact with each other at much lower solid contents than will larger ones. In addition, the particles in a perfectly monodispersed latex will enter into contact at solid contents of approximately 60%, regardless of the ionic strength of our stabilisation system.

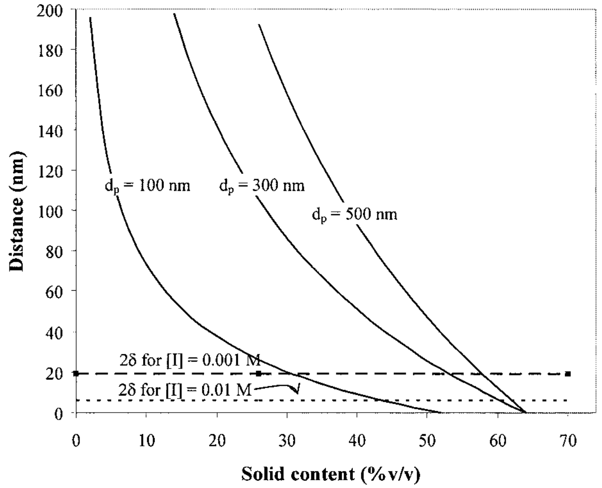

Figure 1. Distance between neighbouring particles for three different monodispersed latices, and 2 times the thickness of the electronic double(2δ) for two different ionic strengths.

These order-of-magnitude results illustrate why most industrial processes with relatively narrow particle size distributions usually operate at less than 55% solids. If one wishes to overcome this limitation, it is clear that the particle size distribution (PSD) of the final latex CANNOT be monodisperse, and probably not even monomodal. The questions that must be asked is therefore how do we best use the space in a latex to: (1) increase the solid content; (2) maintain low viscosity (i.e. minimise interaction between neighbouring particles)? These points are illustrated in the schema shown in, where the principle is to fill the interstices between the large particles with smaller ones, or to reduce the volume occupied by these interstices by adjusting the PSD.

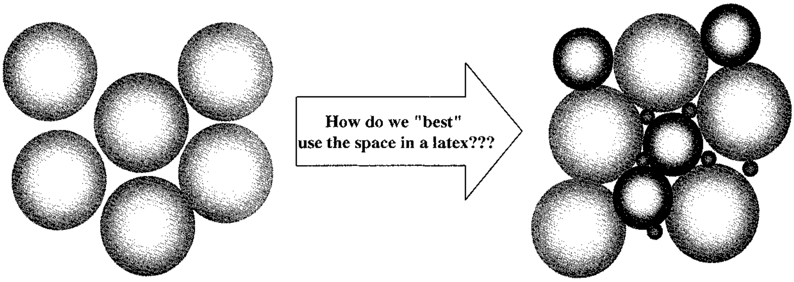

Figure 2. Illustration of the concept of increasing the solid content through the use of a latex with a polydisperse PSD.

The production of high solids content latexes has been treated in the open literature for less than 10 years[1,2,3,4,5,6,7,8,9,10,11] (much longer in the patent literature). Discussions of the relationship between the viscosity and the PSD can be found in some of these texts[[7,8,10,11]]. A recent review article took an in-depth look into the different processes used to make high solid content, low viscosity lattices, as well discussing the relationship between the PSD and viscosity[12]. At the risk of oversimplifying the results in reference [12], the general conclusions from the academic studies are (1) that there are two basic means of creating a multimodal concentrated latex; (2) Most authors attempt to accomplish the goals of low viscosity and high solid by creating bimodal PSD. The processes used to do this are shown in the schema in Figure 3, and are usually similar with the major difference lying in how the second population of particles is generated:

1. **Process 1**: Mixture of two or three monomodal seeds with well defined PSD, followed by a period of growth in a semi-batch reactor.

2. **Process 2:** Creation of a seed latex, with growth of the seed latex particles during a semi-batch reaction followed by one or two nucleations of secondary (and eventually tertiary) populations.

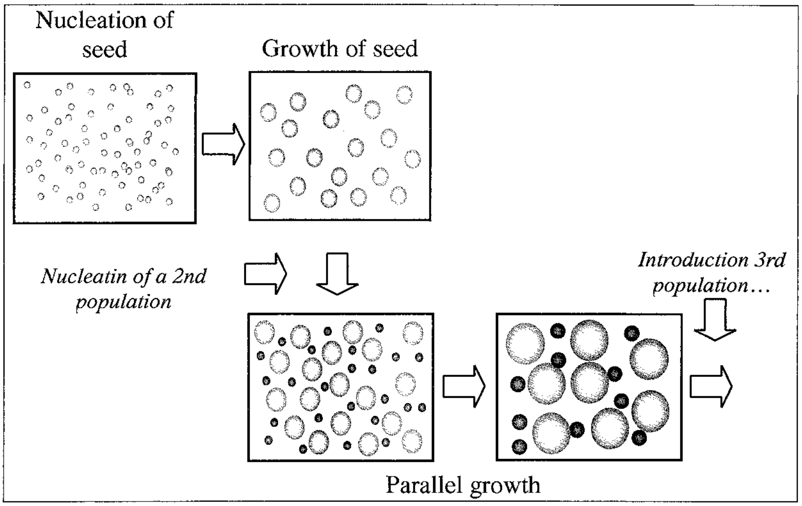

Figure 3. Schema of the process used to make high solid content, low viscosity latex.

The most important point seems to be reproducible control over the PSD of the latex. Creating too many small particles leads to irreproducibility, high viscosity and eventual loss of latex stability (most likely due to a rapid distribution of the surfactant in the system). Secondary nucleation in the presence of water soluble monomers must be also be suppressed since too many fine particles lead to significant increases in the latex viscosity. This can be done by using non-ionic initiators, or oil-soluble initiators. It has been pointed out in the past [8,9] that when a non-ionic initiator (i.e. one that does not generate electrically charged radicals) such as the redox pair H_2O_2/Ascorbic Acid (HPO/AscA) is used to polymerise partially water soluble monomers such as acrylic acid and methyl methacrylate, significantly fewer fine particles are generated. When this is the case, the viscosity of the final latex remains low. In other words the presence of too many fine particles (defined as having diameters more than 8-9 times smaller than the average diameter of the largest particles) is detrimental to the rheological behaviour of the latex.

Process 1 can be used to reach fairly high solid contents using concentrated seeds that are added at well-defined points during the reaction. However doing so implies the production and storage of intermediate seeds, and inevitably leads to the slight dilution of the seed population of large particles since small seeds are going to contain at most 50% polymer per unit volume. While these are not fatal problems, it is desirable to avoid such obstacles from an industrial point of view. On the other hand, it is clear from the literature that nucleating particle populations in situ using shots of initiator(s) and monomer often led to destabilisation of the latex, again, probably due to an extremely rapid generation of surface area and a redistribution of surfactant that destabilised the seed latex.

In this work, we will present a process (type-Process 2) that will allow us to overcome the obstacles mentioned above, and to produce a latex with solid content of over 75% at low viscosity.

Experimental procedures and techniques

The monomers used in this study were methylmethacrylate (MMA) and butyl acrylate (BA); the initiators were ammonium persulphate (APS), and HPO/AscA. These products were obtained from ACROS (Isle, d'Abeau, France) and used as received. The anionic surfactant (TA) used in this study 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 were characterised by Schneider et al.[8]

All reactions were carried out in a 3 litre, jacketed glass reactor connected to heated water bath for temperature control. The reaction temperature was 75°C. Samples were occasionally withdrawn through a valve in the bottom of the reactor for analysis. Conversions were measured by gravimetry. Average particle sizes were measured by Quasi-elastic light scattering (QELS) with a Malvern Lo-C, or by static light scattering using a Beckman-Coulter LS-230 (also used for full PSD). Average particle sizes reported here are averages of 10 measurements per sample, whereas the PSD is an average taken over three measurements of the same sample. Viscosity was measured using a Rheometric Scientific Viscometer (RFS III) at room temperature.

Table 1. Creation and concentration of large particles (Steps 1 and 2)

Initial Charge	
Reactants	**Mass (g)**
H_2O	196
MMA	10
BA	90
TA *Active matter*	*0.005*
Water	*0.011*
TN *Active matter*	*0.89*
Water	*1.34*
H_2O_2	0.86

Feed Streams	
Stream 1. TN	**Mass (g)**
Active matter	6.6
water	70.5
Stream 2. AscA	
Active matter	0.66
water	12.5
Stream 3. Monomer	
MMA	75.7
BA	302.8

Latices were prepared by first polymerising an initial population of large particles to a solid content of approximately 60% (first two steps of Figure 3), then nucleating a second population by in situ nucleation (third step), and then concentrating the latex (fourth step). The recipes (per one hundred grams of monomer) used for the nucleation and concentration of the large particles is given in Table 1, and that used for the steps 3 and 4 is given in Table 2. The batch polymerisation step (Step 1) lasted 120 minutes, and the semibatch concentration step (Step 2) lasted for approximately 330 minutes. Streams 2 and 3 were added at constant flow rate, and Streams 1 and 3 were added only during the semi-batch phase, whicle the AscA was added from the beginning of the batch.

The flow rate of TN (Stream 1) varied slightly as a function of time, and was calculated as follows. At the end of the batch period we have a polymer content of 20% per unit volume and approximately $2.5*10^{16}$ particles / kg with a diameter of 250 nm. The surface coverage (θ) is much lower than 100% (generally closer to 50%) and the latex is stable. This state of colloidal stability (dp, Np, θ) is an equilibrium determined by the system. (It should be pointed out that the surface coverage is calculated assuming that the total amount of surfactant is located on the particle surface, which, strictly speaking, is not the case so the surface coverage calculated in this manner is an upper limit). During the semi-batch step we want to avoid the presence of free surfactant molecules, and above all the formation of micelles. We therefore add just enough TN during the semi-batch phase to just cover the new surface generated by particle growth. The increase of the surface area is calculated assuming that the number of particles remains constant.

Table 2. Recipe used for generation and concentrating small particles (Steps 3 and 4)

Charge	
Reactants	**Mass (g)**
Polymer (Table 1)	100
H_2O	69.5
TA *Active matter*	*0.0012*
water	*0.0025*
TN *Active matter*	*1.77*
water	*0.95*
AscA	0.15
H_2O_{2*}	0.20

Feeds	
Reactants	**Mass (g)**
Shot 1 at t=0	
TN Active matter	0.026
TA Active matter	0.048
water	1.56
Shot 2 at t=0	
APS	1.28
H_2O	2.55
Stream 4. TN	**Mass (g)**
Active matter	6.41
water	13.3
Stream 5. Monomer	
MMA	44.0
BA	175.9

We know that this will not be the case since experience shows that there can be a limited amount of auto-flocculation and the number of particles per litre (N_p) can decrease. However since N_p decreases only a little, we manage to maintain the surface coverage at levels between 60 and 100%, which in turn means that we should not favour situations where homogeneously nucleated particles will be rapidly stabilised . The aim of this procedure is to keep the system in an ***auto-regulated*** state which will allow us to obtain the required distribution of large particles. At the beginning of Step 3, shots of a mixture of TN and TA (Shot 1), and of APS (Shot 2) are added. The different solutions are then fed in as a function of time. Streams 4 and 5 were added at a constant rate. Note that all of the experiments discussed in the present paper will have the same relative compositions (some might have slightly larger or smaller absolute quantities). For the sake of brevity, only the recipes in Tables 2 and 3 are presented – any deviations from these values and flow rates will be discussed on a case-by-case basis. In addition to satisfying the double objective of high solids and low viscosity, any process that is to be useful must be reproducible, so all experiments were run at least twice.

Results and Discussion

The evolution of the number of particles determined from the average particle diameter provided by Malvern Lo-C for the semi-batch portion of the large particle polymerisation (Step 2) in two experiments is shown in Figure 4. Also, the final average diameter is indicated on the graph for both experiments. At 300 minutes, for run E2.310, we can see a sharp increase of the number of particles followed by a strong decrease. This result, and its absence in run E2.314 allow us to deduce some important points in the production of this seed. It should be noted that a small difference exists between E2.310 and E2.314: in the former, TN was added at a constant flow rate, whereas it was added at a time-varying flow rate for E2.314. The differences are shown in Figure 5.

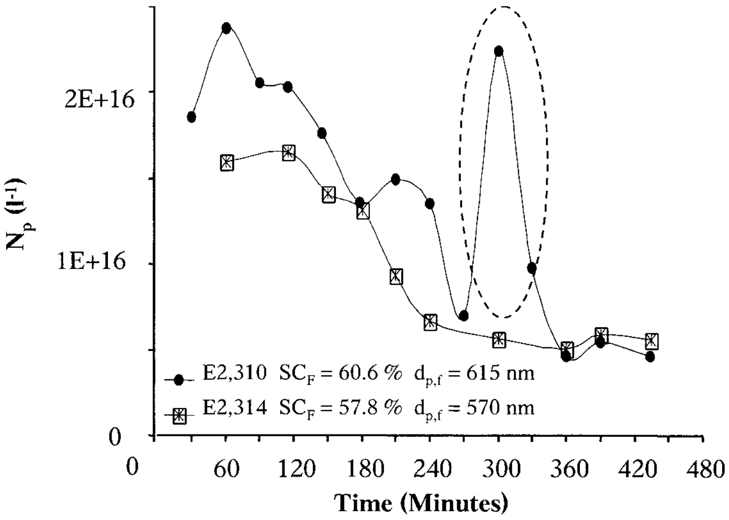

Figure 4. Evolution of N_p for two similar runs (semi-batch, Step 2).

The results in Figure 4 show that particle nucleation occurred during run E2.310, but that the particles created in this manner were not permanently stabilised. In effect, the use of the electrically neutral initiator HPO allowed us to avoid stabilising the fine particles noted by

Schneider et al.[9] when they tried to create seeds in the presence of APS (they suggested that the negatively charge sulphate radicals aided in the stabilisation of small particles). Note that we do not observe the same evolution of N_p for run E2.314. This does not mean that the phenomenon does not occur, but nucleation and auto-flocculation are very fast phenomena. Since samples were only withdrawn every 30 minutes, and the small particles generated in E2.310 flocculate on the larger bodies in the reactor in less time than this, it is quite possible that even if such an event occurred, we might not have been able to measure it.

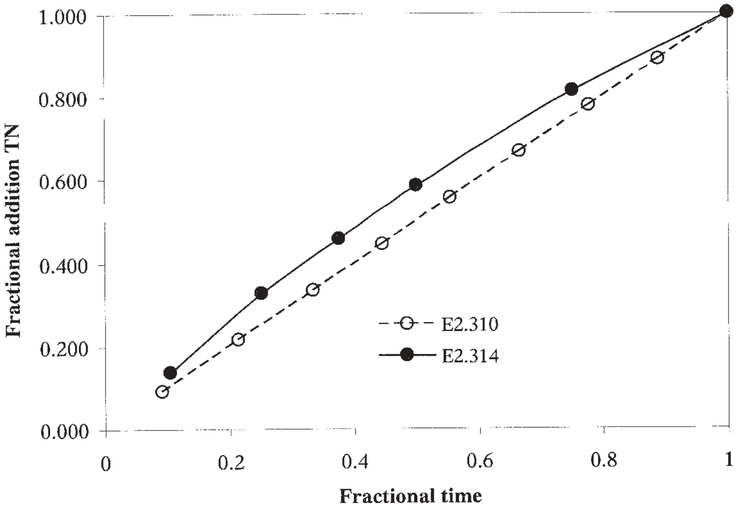

Figure 5. Fractional addition of the non-ionic surfactant solution during runs E2.310 and E2.314.

The PSD of the latices at the end of Step 2 are shown in Figure 6. Two observations can be made here. First of all the two experiments are quite reproducible in terms of the PSD. Secondly, it would appear that the PSD is bimodal, with a limited number of objects on the order of 1.2-1.5 microns being seen. Note that this graph is presented as a volume distribution, which means that in terms of the number of objects, the peak of large particles would not be important. If the end-use of the latex (e.g. as a pressure sensitive adhesive) can tolerate the presence of particles this size, then this in itself is not a problem (in terms of stability and viscosity) since it is essential to avoid the formation of fines. Finally, the rates of polymerisation (R_p) are shown in Figure 7. Here we can see the process is also reproducible in terms of the kinetics, and that the effect of renucleation seen in Figure 4 had no observable effects on the rate (calculated from the derivative of the conversion-time data).

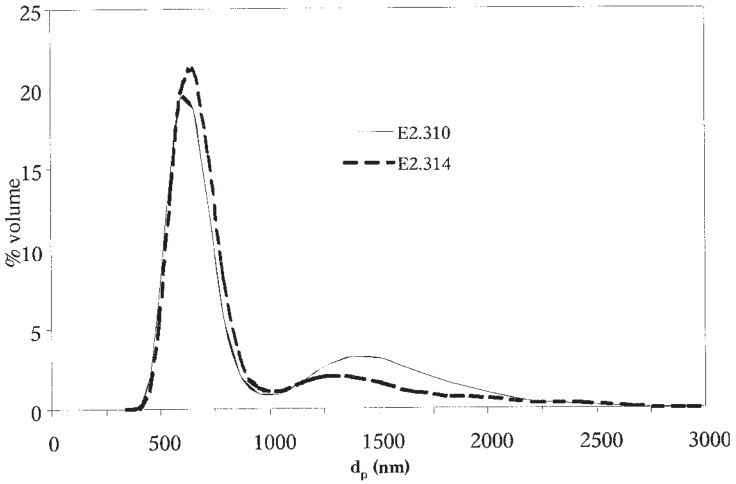

Figure 6. PSD of the two seed runs (Beckman Coulter LS230).

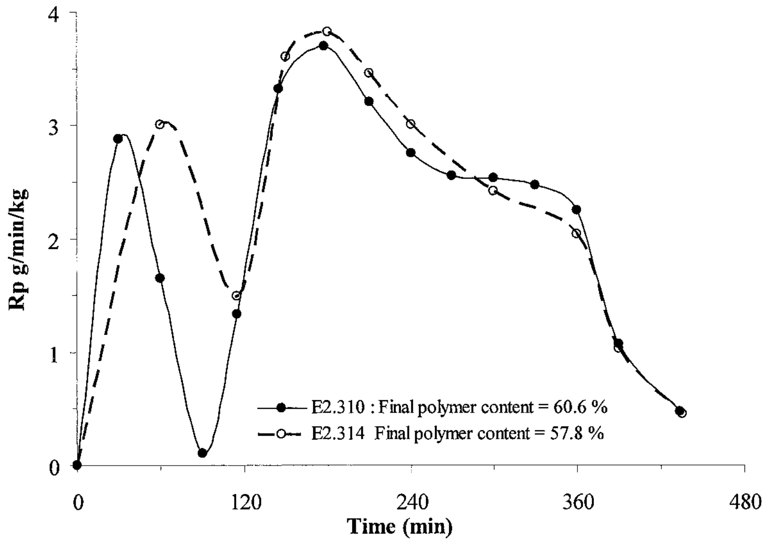

Figure 7. Kinetics of polymerisation during large particle nucleation and growth.

The recipe used here allowed us to reach the required granulometry with a polymer content about 60% in 7 hours. For comparison, Schneider et al. [8] needed more than 10h to reach 50% polymer content with particles of a similar size. This results leads us to believe that the controlled flocculation, brought about by the lack of charges on the surface of homogeneously nucleated particles avoid problems related to their stabilisation, and thus decrease the reaction time. Hence, autoflocculation is a very useful phenomenon if it is controlled. The reproducibility of our process proves that we control the autoflocculation through the use of the initiation system, and means that we can rely on the auto-regulation of the system.

The ultimate objective of this work is to achieve the synthesis of a concentrated latex by an unseeded process. This is achieved by nucleating a second population of particles through the judicious use of a mixture of surfactants, and of a different initiator in Step 3 mentioned above. The results E3.24 and E3.25 represent Steps 3 and 4 in the process, run using the recipes given in Table 2. Recall that in the first half of the production process we used an electronically neutral initiation system to avoid stabilising the small particles generated by homogeneous nucleation.

In this portion of the process we want to stabilise these particles at a reasonable rate.

It appears that most of the difficulties encountered by authors of the studies cited above when they tried to renucleate particles in situ were due to the destabilisation of the latex. It is likely that this destabilisation is due to a very rapid generation of high surface area since the new particles would be very small, but numerous. This in turn led to massive redistribution of the surfactant, some of which came from the surface of the particles already present in the reactor thereby causing them to flocculate. Thus the strategy we adopted here is to inject a very small amount of TA (since without it we cannot renucleate particles with reasonable amounts of TN), and to use APS as the initiator. By adjusting the flow rates of the APS and TN streams, we can maintain a stable rate of nucleation of particles and find a compromise between the kinetics of the stabilisation of the freshly created surface (i.e. the diffusion of surfactant molecules from the water to the surface of the particles) and those of the generation of the surface by nucleation (not too fast, not too slow…). These points are to be treated in detail in two forthcoming papers from this group.

The results are shown in Figures 8-10. It can be seen that the approach proposed here is highly reproducible in terms of the kinetics (Figure 8), the PSD (Figure 9) and the rheological properties of the latices (Figure 10, here diluted to the same polymer contents). While the final latices do not have bimodal PSD in the strictest sense, it is clear that the seed population grows a little, but that we also manage to create a fair number of small particles through controlled nucleation and stabilisation. In any event, the process is clearly reproducible, and the generation of a second population of small particles in this manner allows us to make latices with very low viscosities at quite high solid contents.

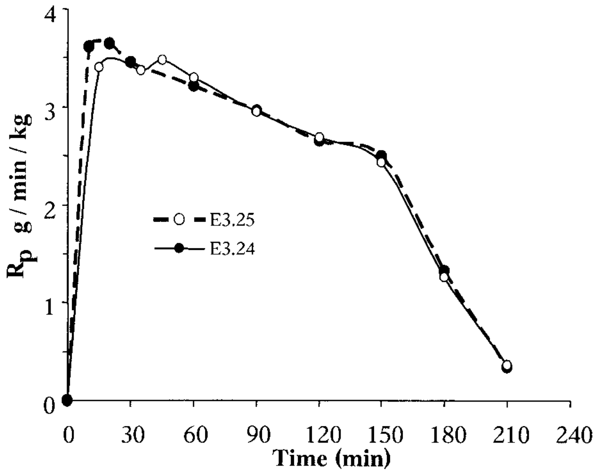

Figure 8. Rates of polymerisation of Steps 3 and 4 for 2 runs using the same initial latex (step 2).

Note that the surfactant concentration in this portion of the reaction remains very close to the critical micelle concentration throughout Steps 3 and 4. This is one of the keys to the reproducibility of the PSD in this portion of the experiment. The flow rates chosen here are intended to keep the surfactant at these minimum levels so as to avoid forming a large number of small particles very rapidly by micellar nucleation. It is believed that most of the particles nucleated here are in fact formed from homogeneously nucleated particles that are stabilised by a combination of electrostatic stabilisation due to the presence of the negatively charged sulphate groups on the chain ends that are localised on the surface of these particles combined with low levles of TA, and eletrosteric stablisation due to the presence of the TN in the reactor. More results are needed to verify this hypothesis.

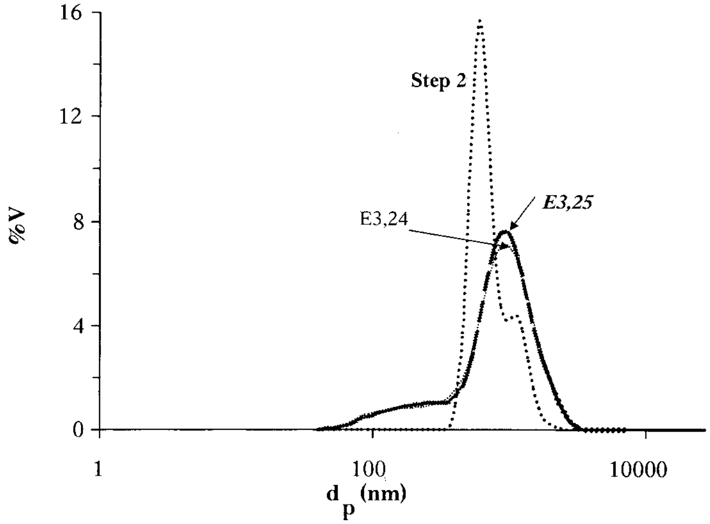

Figure 9. PSD of the latex and the end of Step 2, and o E3.24 and E3.24.

Conclusions

The work presented in this paper demonstrates that it is feasible to produce high solid content, low viscosity latices via a process based on in situ nucleation. The use of an electrically neutral initiator and a judicious choice of surfactants in the first step allowed us to avoid stabilising fine particles in the initial portion of the process. Limited flocculation of the small particles formed by homogenous nucleation (due to the presence of MMA) contributes to a relatively rapid growth of the large particles in the first stages of the process. In addition the fact that they are not stabilised contributes to a fairly low intermediate viscosity.

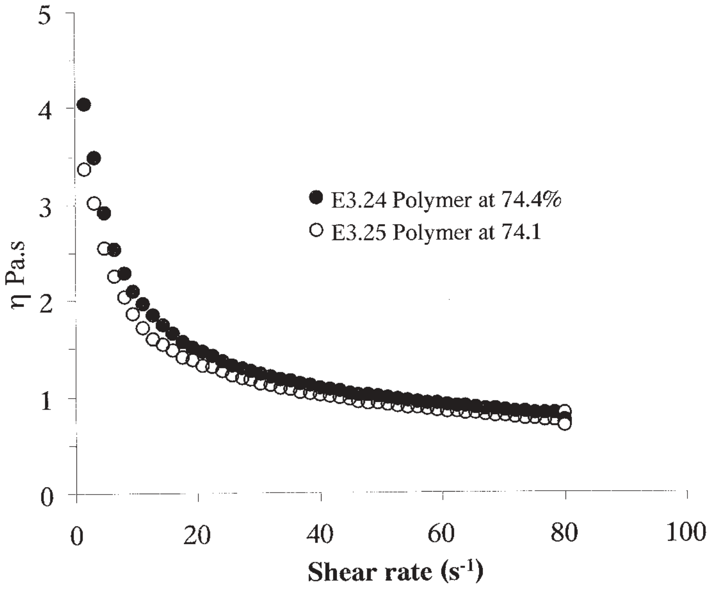

Figure 10. Viscosity as a function of shear rate for the two latices at 74% polymer.

Switching to a persulphate initiator in the second half of the process while maintaining low levels of surfactant in the reactor allowed us to stabilise a portion of the homogeneously nucleated particles, thereby leading to the formation of a population of small particles. The process proposed here was shown to be highly reproducible. Future work will focus on the effect of including functional monomers such as acrylic or methacrylic acid, and on deepening our understanding of the physical and chemical processes involved in particle formation.

Acknowledgements

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