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Factors affecting kinetics and coagulum formation during the emulsion copolymerization of styrene/butyl acrylate

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Abstract

The effect of the agitation rate, feeding time, initiation rate and latex viscosity on coagulum formation in the emulsion copolymerization of styrene and butyl acrylate under industrial-like conditions was investigated. The results were analyzed using computational fluid dynamics to simulate the flow pattern in the reactor. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Agitation; Emulsion copolymerization; Computational fluid dynamics

1. Introduction

Emulsion polymerization is currently the predominant process used in the industry to produce a great variety of polymers with multiple uses (paints, adhesives, coatings, binders,…) [1]. Because of its multiphase and compartmentalized nature, emulsion polymerization offers the possibility of preparing polymers with unique properties that cannot be produced by other polymerization techniques. In addition, environmental regulations have led to the substitution of solvent-based polymers by water-borne latexes, increasing the importance of emulsion polymerization. Agitation plays a key role in the process because it affects the emulsification of the monomers, the mass transfer between droplets and particles, the nucleation and coagulation processes and the heat transfer.

In many latex applications like paints, adhesives or leather processing a high solid content is required. In other cases when the interest is in the polymer dispersed in the latex, the high solid content allows to lower the price of some operations like transport and evaporation of the water. Although in the industry, solids content higher than 50% are very common [2–5], most of the studies on agitation have been done with low solid-content latexes [6–11], the studies on the effect of the agitation on high solid-content latexes being very scarce [12–15]. Vanderhoff [12] proposed two mechanisms for the formation of coagulum in emulsion polymerization: (i) failure of the colloidal stability of the latex during or after the polymerization, to cause coagulation of the particles and formation of microscopic or macroscopic coagulum; (ii) polymerization of the monomer by a mechanism other than that of emulsion polymerization, to give polymer in a bulky form. Lowry et al. [13,14] studied the mechanical coagulation in emulsion polymerization correlating its formation with some agitation parameters. For low Reynolds numbers, the rotational speed was important, whereas for high Reynolds numbers, power consumption was the important parameter. Matejicek et al. [15] found that increasing mixing intensity improved the temperature and concentration homogeneity, which resulted in the decrease of coagulum content. However, from a certain value of mixing intensity the amount of coagulum started to increase due to increasing shear stress.

At least two fundamental problems appear with high solid-content latexes. One of them is maintaining the colloidal stability of the polymer particles when the frequency of the collisions between these particles is high. The other is that the latex viscosity increases with the solids content. This affects the heat transfer and the mixing.

The agitation affects the colloidal stability, the heat transfer and the mixing. It even has a certain effect on viscosity because latexes with solid contents higher than 40% have a pseudoplastic behaviour [16,17], i.e. viscosity decreases as shear rate increases. Unfortunately, agitation has conflicting effects. Thus, an increase of the agitation improves the mixing and the heat transfer, but it also increases the frequency of the collisions between particles and the energy

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Table 1
Recipe used in polymerizations A1–A4 carried out at agitation speeds of 70, 100, 150 and 220 rpm, respectively ($T = 70$°C)

	Initial charge (g)	Stream 1 (g)	Stream 2 (g)
Styrene	50.9	–	458.1
Butyl acrylate	41.8	–	375.8
Acrylic acid	0.93	–	8.4
SLS	2.8	11.1	–
Antarox CO630	1.9	7.4	–
$(NH_4)_2S_2O_8$	3.7	14.8	–
DDI water	160.0	640.0	–
Flow rate		2.34 g/min	1.86 g/min

of each collision, causing coagulation. This is undesirable because it gives macrocospic coagula, which results in lower productivity, or in an increase of the average size of the particles, which in turn yields a lower product quality when a small particle size is required.

This suggests that there is a range of agitation intensity that allows a good mixing of the system and an effective elimination of the polymerization heat without causing a significant coagulation. Nevertheless, there is no way to predict the existence of this zone of optimal agitation or, in case it exists, the range of values of the agitation speed. Since this range can depend on the system under study, in these series of papers it has been decided to study three systems which are representative of the latexes used in paint production: styrene–butyl acrylate, vinyl acetate–VeoVa10 (the VeoVa10 is a vinyl ester of the Versatic10 acid, Shell trademark, that is a blend of graft isomers of 10 carbon atoms [18]) and vinyl acetate–butyl acrylate. These monomers are characterized by their different reactivity and water solubility: (styrene (0.06 g/100 g of water) [19], butyl acrylate (0.14 g/100 g of water) [19], vinyl acetate (2.5 g/100 g of water) [19]), which likely affects mass transfer and polymerization kinetics.

The study was carried out in conditions similar to those of the industry, that is to say, a semicontinuous process, high solid content (55%) and technical monomers. The effect of the agitation on the mixing (mass transfer) and on the coagulation was studied. The heat transfer was not studied since the polymerizations were carried out in a laboratory reactor (2 l), which owing to its small size has a large heat transfer area/volume ratio and it removes the heat very efficiently.

In this paper the effect of the agitation on the emulsion polymerization of styrene/butyl acrylate is presented. The results corresponding to vinyl acetate/Veova10 and vinyl acetate/butyl acrylate monomer systems will be presented in following papers.

Table 2
Recipe used to produce the seed ($T = 80$°C)

	Weight (g)
Styrene	28.0
Butyl acrylate	23.0
SLS	2.0
$(NH_4)_2S_2O_8$	2.7
$NaHCO_3$	2.0
DDI water	1651.0

2. Experimental

Three series of reactions using styrene and butyl acrylate as monomers were carried out. The first series (series A, reactions A1–A4) corresponded to ab initio (unseeded) emulsion copolymerizations carried out using a thermal initiator and with agitation speeds of 70, 100, 150 and 220 rpm, respectively. The second (B) and third (C) series were seeded emulsion copolymerizations initiated with a redox initiator. Different initiator concentrations and feeding times were used in series B and C. In series B 2 wt% of initiator based on monomers and a feeding time of 6 h were used, whereas in series C 1 wt% of initiator and a feeding time of 3 h were used.

The recipe used in series A is shown in Table 1. Technical grade monomers, i.e. containing inhibitors (*p*-tertbutylcathecol 10 ± 5 ppm in styrene and *p*-methoxyphenol 50 ± 10 ppm in butyl acrylate), were used. Sodium lauryl sulfate (SLS, Merck 90%) was used as anionic emulsifier and Antarox CO630 (ethoxylated nonylphenol, 63 moles of poly(oxyethylene), Rhodia) as nonionic emulsifier. Ammonium persulfate ($(NH_4)_2S_2O_8$, Merck 90%) was used as thermal initiator. Deionized water was used throughout the work. In the recipe a small amount of acrylic acid (AA) (1 wt% referred to the total monomer) was included. The use of small amounts of polar monomers is common practice since they increase the latex stability and the adhesion onto substrates.

The procedure used in these polymerizations was as follows: 10% of monomers and 20% of the remaining recipe components, except the initiator and a small portion of water necessary to dissolve it, were initially charged in the reactor. The system was heated until the temperature of reaction (70°C) and 20% of the initiator was added as a shot. The system was allowed to react in batch for 15 min, and then the two feed streams were fed during 6 h. Subsequently, the polymerization was continued in batch for 1 h. As will be presented in Section 3, the conversions reached in the first series of reactions (series A) were low, and hence, it was decided to use a seed to increase the number of polymer particles and a redox initiator to increase the radical flux.

A seed was prepared in a batch reactor at 80°C using the recipe given in Table 2. This seed (dp ≈ 30 nm, solids content ≈ 3.3 wt%) was included in the initial charge of series B and C, which were carried out following the recipe given in Table 3, with agitation speeds of 100 (B1 and C1), 150 (B2 and C2) and 220 rpm (B3 and C3). In these polymerizations, Arkopal N230 (ethoxylated nonylphenol (23 moles of PEO, Hoechst) as nonionic emulsifier and SLS as anionic emulsifier were used. The use of a mixture

Table 3
Recipe used in series B and C. Series B: 2 wt% of initiator and 6 h of feeding time. Series C: 1 wt% of initiator and 3 h of feeding time

	Initial charge (g)	Stream 1 (g)	Stream 2 (g)	Stream 3 (g)
Styrene	–	–	–	474.3
Butyl acrylate	–	–	–	389.1
Acrylic acid	–	–	–	8.7
SLS	3.5	9.3	–	–
Arkopal N230	2.3	6.4	–	
$(NH_4)_2S_2O_8$	–	–	8.7/4.3	–
$Na_2S_2O_5$	–	8.7/4.3	–	
Seed	200.0	–	–	–
DDI water	200.0	178.5	179.2	–
Flow rate				
Series B		0.56 g/min	0.50 g/min	2.42 g/min
Series C		1.10 g/min	1.02 g/min	4.84 g/min

Run	Agitation rate (rpm)
B1/C1	100
B2/C2	150
B3/C3	220

of ionic and nonionic emulsifiers is common practice, because the ionic emulsifier stabilizes the latex particles better during the rapid increase in surface area occurring in the first stages of the process, and the nonionic emulsifier increases latex stability against electrolyte addition. The polymerization was initiated using a redox system: ammonium persulfate/sodium metabisulfate. Technical grade monomers were used. The emulsifiers and the initiators were used as received. Series B used 2 wt% of initiator and a feeding time of 6 h. Series C used 1 wt% of initiator and a feeding time of 3 h.

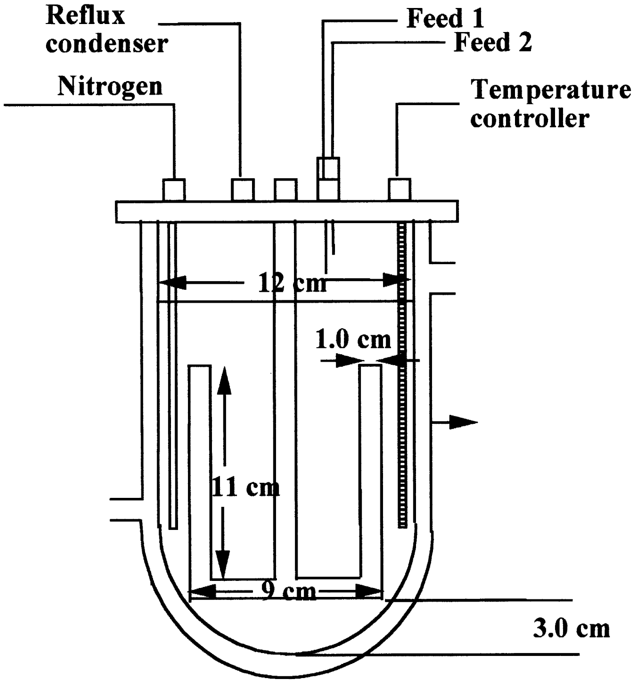


Fig. 1. Reactor.

Polymerizations were carried out in a 2-l glass reactor fitted with a reflux condenser, stainless steel anchor stirrer, sampling device, nitrogen inlet and feed inlet tubes. Dimensions of the reactor and the agitator are shown in Fig. 1. The seed and an aqueous solution of the emulsifiers were initially charged into the reactor. The system was heated to 70°C and the feed streams were added during 3 or 6 h. The ammonium persulfate stream was maintained during 15 min after the end of the monomer feeding to achieve the complete conversion of the monomer fed [20].

Samples were withdrawn from the reactor at appropriate intervals and polymerization was short-stopped with hydroquinone. The conversion was determinated gravimetrically. The particle size of the latex was measured by dynamic light scattering (Coulter N4 Plus from Coulter Corporation, Fullerton, USA). At the end of the process, a sample was withdrawn to determine the particle size distribution (PSD) by disc centrifuge photosedimentation (BI-DCP from Brookhaven Instruments Corporation, Holtsville, USA).

After polymerization, the final latex was filtered through a filter of 63 mesh, and the coagulum retained was collected together with that deposited in the reactor walls, agitator and sampling tube. The dry weight of these coagula related to the total monomer was defined as the coagulum percentage. Coagulum is undesirable because it results in a reduction of the solids content, and it might reduce productivity as longer reactor cleaning operations are required. In addition, limited coagulation leading to larger particle sizes may cause a negative effect on the properties of the latex.

3. Results and discussion

Fig. 2 presents the effect of the agitation rate on monomer conversion for series A, carried out with agitation speeds of

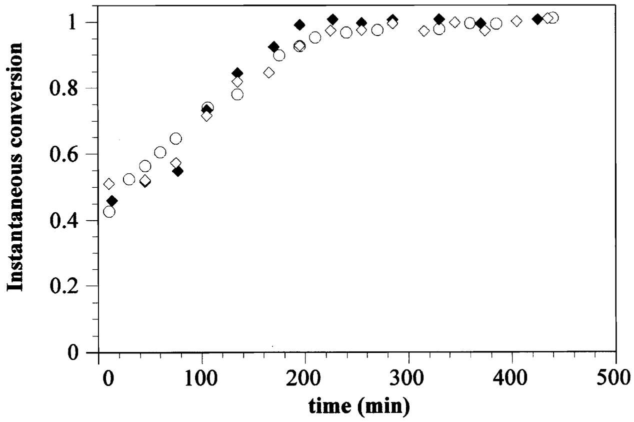


Fig. 2. Effect of the agitation rate on monomer conversion in series A: (○) $N = 100$ rpm (A2), (◆) $N = 150$ rpm (A3), (◇) $N = 220$ rpm (A4).

100 (run A2), 150 (run A3) and 220 rpm (run A4). It can be seen that in this range of agitation rates, monomer conversion was not affected by agitation rate. However, in the polymerization carried out with the same recipe at 70 rpm (run A1), the formation of a monomer layer was observed in the liquid surface. This indicates that the monomer was not efficiently transported to particles, probably because the agitation speed was not intense enough to finely disperse the monomer in the system. This run could not be completed because a large amount of coagulum was formed. The coagulum was mainly formed by the polymerization of the monomer accumulated in the liquid surface, namely, formed by bulk polymerization and not by emulsion polymerization.

The amount of coagulum (in wt% referred to total monomer) obtained in reactions A2–A4 is presented in Fig. 3. It can be observed that an appreciable amount of coagulum was found at 100 rpm whereas almost no coagulum was observed at higher agitation rates. Combination of these results with that obtained at 70 rpm (severe coagulation) suggests that 100 rpm is close to the minimum agitation speed required to ensure the emulsification of the entering monomer, avoiding the formation of a layer of monomer at the liquid surface. An increase of the agitation speed beyond 150 rpm did not result in a further reduction of the coagulum percentage.

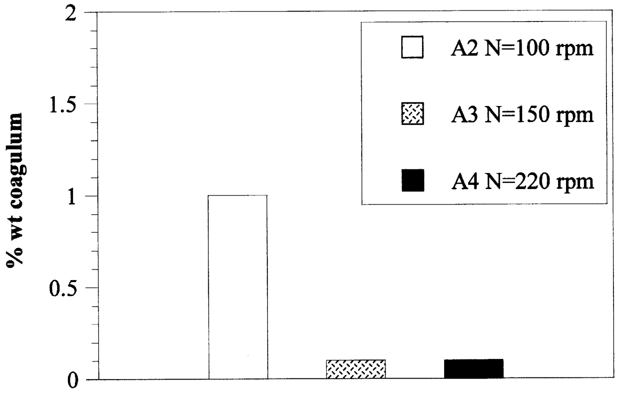
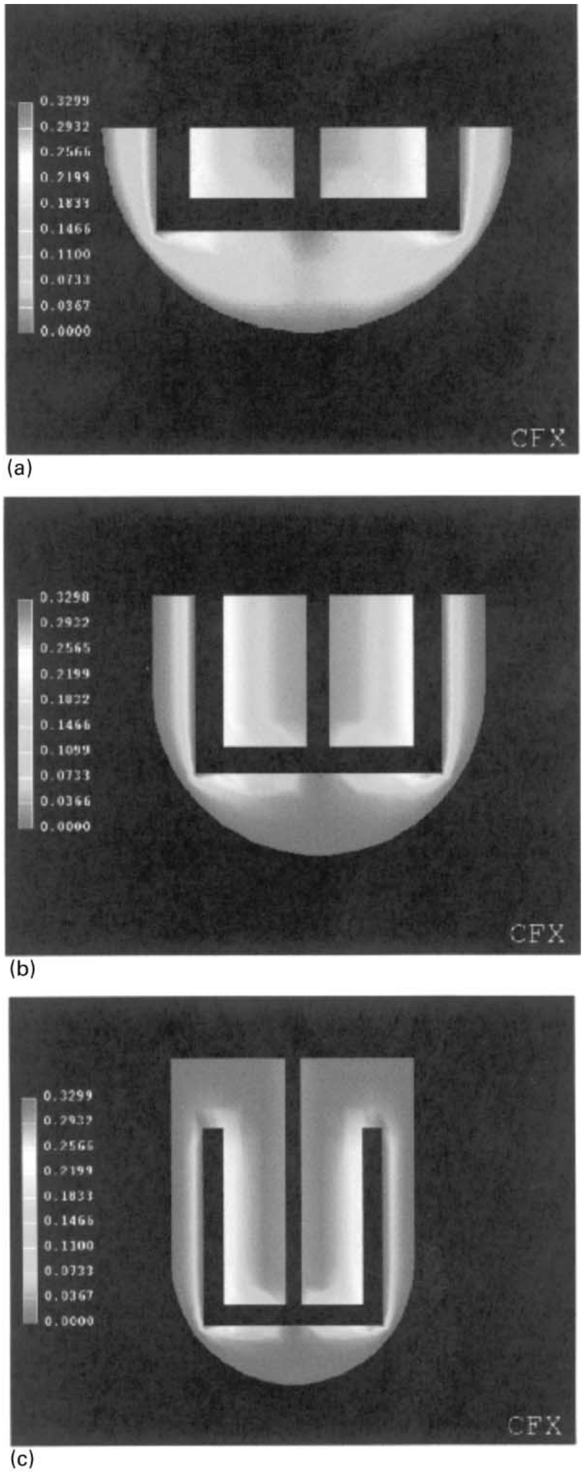


Fig. 3. Percentage of coagulum obtained in the reactions A2, A3 and A4.



(a)

(b)

(c)

Fig. 4. Velocity pattern in the reactor calculated by means of computational fluid dynamics for the run A1 (70 rpm). (a) Initial stages of the process; (b) intermediate stages; and (c) end of the process.

The results of coagulation obtained at low agitation speed can be explained analyzing the flow pattern in the

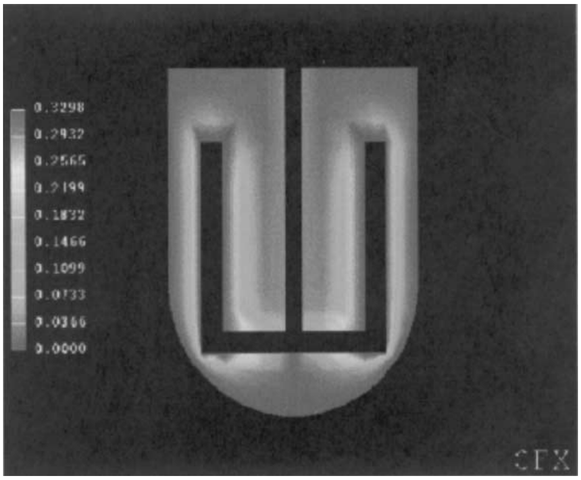


Fig. 5. Velocity pattern in the reactor calculated by means of computational fluid dynamics for the end of run A2 (100 rpm).

polymerization reactor obtained by means of computational fluid dynamics (CFD) using a commercially available computer code [21]. CFD calculations require a rheological model for the system. Because of the continuous increase in solids content, the rheology of the latex varies from a low viscous Newtonian fluid at the beginning of the process to a pseudoplastic rather viscous fluid at the end of the polymerization. For the purposes of this work, three stages of the process were chosen. In all cases, the Ostwald–de Waele equation was used to correlate shear stress (τ) and shear rate ($\dot{\gamma}$) [22].

$$\tau = -K\dot{\gamma}^{n} \qquad (\mathrm{N/m^2})$$

At the beginning of the process, $K = 0.001$ (kg/m s^{2-n}) and $n = 1$. This corresponds to a Newtonian fluid of viscosity = 1 mPa s. At the intermediate stages of the process, $K = 4.8$ (kg/m s^{2-n}) and $n = 0.8$, which corresponds to a slightly pseudoplastic fluid. For the final stages of the process, $K = 24.0$ (kg/m s^{2-n}) and $n = 0.2$, which represents a strongly pseudoplastic system.

Fig. 4 presents the velocity pattern calculated for the reactor at different stages of the polymerization process carried out at 70 rpm. Fig. 4a corresponds to the initial stages of the reactor. In this figure, the dark color corresponds to regions of low velocity and the light color to high-velocity regions. It can be seen that at the beginning of the process the content of the reactor is fairly well mixed with almost no stagnant zones. Fig. 4b corresponds to intermediate stages of the process. Because of the increase of the solids content, the viscosity has increased, and this has a significant effect on the velocity pattern. It can be seen that the region of slow fluid motion has increased substantially as compared with Fig. 4a. Fig. 4b shows that around the agitation shaft and close to the reactor walls stagnant zones are formed. These are the regions where monomer accumulation takes place. The situation is aggravated toward the end of the process when viscosity reaches its maximum value and the agitator is below the surface of the reaction mixture (Fig. 4c). The presence of the stagnant zones near the surface of the reaction mixture is at the beginning of the formation of coagulum. The monomer, which is fed from the top of the reactor, enters into the reactor through these zones, and it is not emulsified. Under these circumstances, monomer mass transfer to the polymer particles is very slow because of the small interfacial area of the entering monomer droplets. Therefore, the monomer accumulates on top of the fluid forming a separate layer, yielding coagulum upon bulk polymerization.

Fig. 5 presents the velocity pattern calculated by CFD for the final stages of run A2 (100 rpm). Comparison with Fig. 4c shows that the regions of slow fluid motion were reduced significantly when the agitation speed increased to 100 rpm. This allowed a good enough emulsification of the monomer, and hence a substantial reduction of the coagulum.

In series B and C a redox initiator was used with the purpose of increasing the polymerization rate, which in turn would increase the system sensitivity to the monomer diffusion rate from the droplets to the particles. These series of reactions differ in both initiator concentration and feeding time. In series B, 2 wt% of initiator (1 wt% of oxidant and 1 wt% of reductor) and a feeding time of 6 h were used, whereas in series C, 1 wt% of initiator (0.5 wt% of oxidant and 0.5 wt% of reductor) and a feeding time of 3 h were used. The formulations used to carry out these reactions are given in Table 3. The seed used as initial charge in these series was prepared using the formulation given in Table 2.

The reactions B1 and C1, carried out with an agitation speed of 100 rpm, were stopped before the end of the feeding period because a large amount of the coagulum was formed. This suggests that the agitation requirements became more demanding as the initiation rate increased. Coagulum was drastically decreased in series B by increasing the agitation rate to 150 rpm (Fig. 6). The increase of agitation rate also results in a decrease of the amount of coagulum in series C, but the decrease was smaller than in series B. Series C used a higher feed rate. This resulted in a

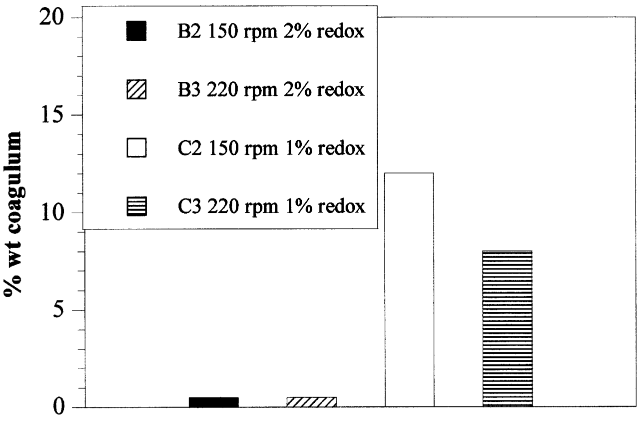


Fig. 6. Coagulum formed in runs B2, B3, C2 and C3.

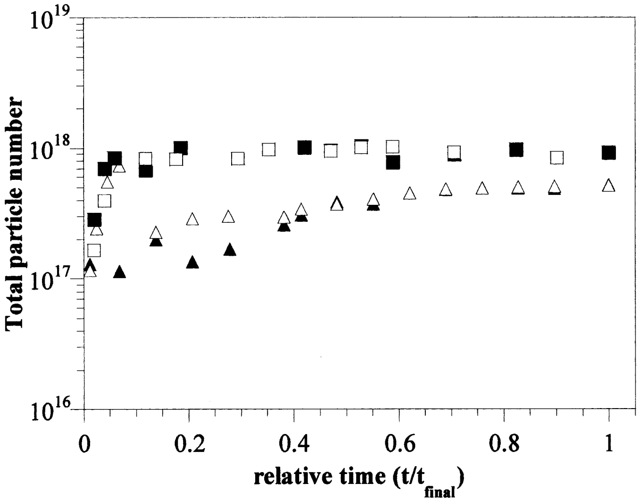


Fig. 7. Time evolution of the total particle number for series B and C: (a) B2 and B3 (2 wt% initiator and 6 h feeding time) — (▲) $N = 150$ rpm (B2), (△) $N = 220$ rpm (B3); (b) C2 and C3 (1 wt% initiator and 3 h feeding time) — (■) $N = 150$ rpm (C2), (□) $N = 220$ rpm (C3).

number of polymer particles higher than in series B (Fig. 7). Therefore, C latexes were much more viscous than B latexes (Fig. 8). The combination of a high viscous reaction mixture and a high feed rate led to monomer accumulation and coagulum formation.

For series B it was found that the agitation rate had no effect on monomer conversion suggesting that 150 rpm are enough to emulsify the monomer efficiently, overcoming diffusional limitations. On the other hand, a relatively large amount of coagulum was obtained in series C.

Fig. 9 presents the PSD of the final latexes from runs B2 and B3 obtained by disc centrifuge. It can be seen that the PSD shows some bimodality which likely resulted from secondary nucleation (small particle size peak) in the presence of seed particles (large particle size shoulder). Other reasons, such as limited shear-induced coagulation, seem to be less plausible as the height of the second shoulder did not increase with agitation rate.

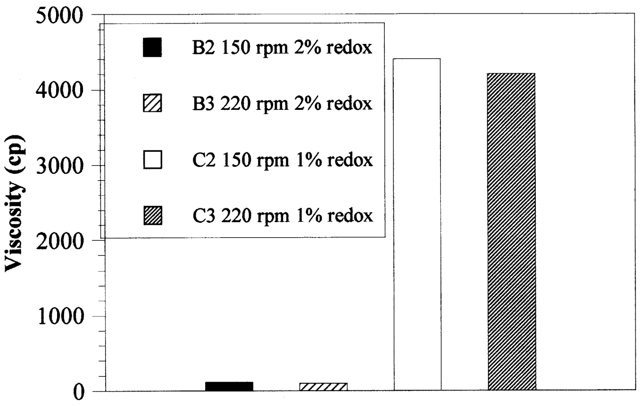


Fig. 8. Viscosity of the final latexes of reactions B2, B3, C2 and C3.

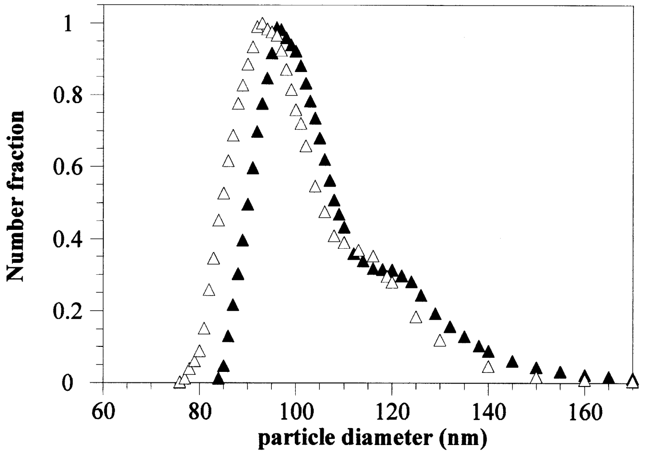


Fig. 9. Particle size distribution of the final latexes for reactions: B2 ((▲) $N = 150$ rpm) and B3 ((△) $N = 220$ rpm).

4. Conclusions

The effect of several variables on coagulum formation in the emulsion copolymerization of styrene and butyl acrylate under industrial-like conditions (technical monomers, 55 wt% solids content and semicontinuous process) was investigated. Both thermal and redox initiations were used. Polymerizations carried out using the thermal initiator proceeded under flooded conditions (relatively low instantaneous monomer conversion). Under these circumstances, a minimum agitation speed was required to emulsify the entering monomer efficiently, avoiding monomer pooling on top of the reaction mixture, which leads to coagulum formation by bulk polymerization. These results were analyzed using computational fluid dynamics to simulate the velocity pattern in the reactor. It was found that large stagnant regions appeared near the agitation shaft and close to the reactor wall. The situation is aggravated toward the end of the process when the agitator was covered completely by the reactor content, because the whole surface of the reaction mixture (where the feed entered the reaction mixture) remained stagnant.

Polymerizations carried out using a redox initiation system showed that the agitation requirements became more demanding as the initiation rate increased. It was also found that the monomer accumulation and coagulum formation increased with the viscosity of the reaction mixture. No proof of shear-induced coagulation was observed.

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