Effect of monomer feed rate on the properties of copolymer butyl acrylate/vinyl acetate in semi-batch emulsion polymerization

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In this work, the effects of the pre-emulsion feed rate on the instantaneous and overall conversion, average particle diameter, particle size distribution, polymer particle concentration, polymerization rate, average number of radicals per particle, viscosity and coagulum of a 65 wt% total solid contents of butyl acrylate/vinyl acetate copolymer latexes during relevant emulsion polymerization over pre-emulsion feeding times of 1, 2, 3, 4 and 6 h were investigated. The temperature of reaction was maintained at 85°C during the feed input and at 90°C for 1 h after the end of the feed. The effect was quite significant for feeding times of 1 to 3 h and it was of minor significance for feeding times varying from 3 to 6 h for the conversion, average particle diameter and polymer particle concentration. The polymerization rate was influenced by the feeding time, while the particle size distribution was not affected by the feeding time. The viscosity and average number of radicals per particle exhibited a clear tendency of inversion at the critical feeding time of 3 h. The coagulum formation decreased with feeding time up to 4 h and increased drastically for 6 h.

Keywords: Co-polymerization, Vinyl acetate, Emulsion polymerization
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One of the most important latexes in the industry is the one of the copolymer vinyl acetate/butyl acrylate (VAc/BuA) with 15 to 25 wt.% of butyl acrylate[1]. This latex is widely used in architectural paint formulations. The copolymer VAc/BuA is characterized by large property differences in respect of reactivity ratios (r_{VAc}=0.05 and r_{BuA}=5.5), water solubility (25 g/L and 1 to 1.5 g/L for VAc and BuA, respectively, at 25°C), propagation rate constants [k_p(VAc)=7000 L/mol.s and k_p(BuA)=400 L/mol.s, both at 85°C] and glass transition temperature [T_g(VAc)=32°C and T_g(BuA)=-54°C]. Due to these significant monomer property differences, the resulting latexes may exhibit wide molecular, morphological and particle properties depending on the copolymer composition that additionally affects, for example, the T_g of the copolymer.

The water solubility differences of the monomers affect their relative partition between water phase and polymer particles. The higher water solubility of VAc makes the polymerization to occur mostly in the water phase for low conversions through the mechanism of homogeneous nucleation. For higher conversions, the total volume of polymeric particles increases and the polymerization occurs mostly in the polymer particles.

Several processes are used in the emulsion polymerization (batch, semi-batch and continuous). Among these processes the most versatile is the semi-batch, although it is not so used as the other types[2]. The most important advantage of the semi-batch process in the emulsion polymerization is its operational flexibility in relation to the batch and continuous processes. In the semi-batch process several variables can be manipulated, e.g., monomer feed (neat, solution or emulsified), initiators, emulsifiers, protective colloid and additives; mechanical agitation (velocity and agitator type); temperature (constant or programmable along the reaction); composition and quantity of the initial charge to the reactor[3].

Semi-batch processes are particularly interesting in emulsion copolymerization for controlling particle morphology and to partly obviate the copolymer composition drift, which is observed in the batch polymerization, mainly because of differences in reactivity ratios and water solubility between the co-monomers, i.e., the VAc/BuA system[4].

In a batch process, this copolymer would be strongly heterogeneous[5]. The same copolymerization in a semi-batch process can produce highly homogeneous copolymer since the co-monomer feed

rate may be lower than the polymerization rate, thereby, giving rise to starved condition[2]. The starved condition is advantageous for the VAc/BuA copolymerization due to the high propagation rate constants, but can lead to extremely long reaction times for systems with relatively low propagation rate constants, for example, the system butyl acrylate/styrene. The feed rates of the co-monomer mixtures have an important effect on the final properties of the VAc/BuA latexes. The instantaneous conversion, the copolymer homogeneity and the average particle diameter increase with the feeding time[6]. The average particle diameter and particle size distribution, PSD are strongly influenced by the co-monomer composition[7] in semi-batch processes. In semi-batch operations, the particle nucleation takes place predominantly in the aqueous phase and the particles are formed over the entire duration of the polymerization process. Particle size growth takes place predominantly by coalescence of smaller particles with larger ones, as well as to a lesser extent by diffusion of co-monomer from the water phase to the growth-centre particles where polymerization occurs. When the co-monomer mixture is rich in the relatively more hydrophilic vinyl acetate monomer, unfavourable adsorption of emulsifier on the particle surface results in a low level of colloidal stability of the newly formed small size latex particles. The coalescence of the smaller particles among themselves or with existing large size particles leads to an increase in the average particle diameter and narrower PSD with the increase in the VAc content in the co-monomer mixture.

The PSD is the most important parameter influencing the viscosity, specially for high solid content emulsions[8]. The viscosity diminishes as the mean particle diameter increases and the PSD becomes broader. The small particles filling the interstices act as lubricants to the large particles, lowering the surface interactions between particles and, consequently, the viscosity. The viscosity also grows with the solid contents as a consequence of the higher surface interactions among the particles. It was observed for the terpolymerization of VAc/MMA/BuA that with the increase of the feeding time from 4 to 6 h, the average particle diameter, measured by dynamic light scattering, increased slightly from 214 to 229 nm[8], but these results were inconclusive because the seeds used were of different particle size and of different concentrations.

The average number of radicals per particle, $\bar{n}$, was not constant for the system VAc/BuA[9], because $\bar{n}$

changed with overall conversion for an initial co-monomer feed composition of 50:50 wt.%. In the initial stage, $\bar{n}$ regularly decreased from 2 to 0.5 as BuA was consumed, then remained practically constant for a period (50-70% approx. conversion) when the BuA amount became low, and, finally, drastically decreased to very low values after BuA has been totally depleted. This fact was related to growing radical events, since the particle number variation was small. Just after BuA disappeared, an increase in the overall copolymerization rate, R_P, was observed due to a pronounced increase in the overall rate constant, k_P, and due to a limited radical transfer reaction impeded by the BuA units in the chains. As the reaction proceeded, the particle surface enriched in VAc units and the behaviour usually encountered with pure VAc emulsion polymerization prevailed, leading to very low $\bar{n}$ values, due to high number of radical transfer reactions. A thorough discussion about polymerization kinetics and modeling are given elsewhere[10].

The amount of coagulum in the end of the copolymerization can cause off-spec products. Coagulum is formed as a consequence of colloidal instability of the latex particles as well as of higher kinetic energy of the particles[11]. In this study the only variable that can affect the coagulum formation is the feeding time. For the same copolymerization recipe, the coagulation rate depends only on the number of latex particles and, therefore, the coagulum amount in the latex should increase with the feeding time.

The study of the 65 wt.% solid content latex miniemulsion copolymerization of butyl acrylate and styrene showed that the co-monomers feeding time had no effect on the amount of coagulum formed[12].

The aim of the present work was to study the effect of the feeding time of a fixed amount of VAc/BuA (80/20 wt.%) pre-emulsion on the properties (instantaneous and overall conversion, polymerization rate, average particle size, PSD, polymer particle concentration, viscosity, average number of radicals per particle and coagulum formation) of the emulsion and copolymer.

Experimental Procedure

Materials

Vinyl acetate (containing 15 ppm hydroquinone) and butyl acrylate (containing 50 ppm MEHQ) of technical grade were supplied by Rhône Poulanc Brazil and used as received without purification; ionic surfactant nonyl phenol polyglycol ether sodium

sulphate ethoxylated with 25 mols ethylene oxide (Disponil 25 S from Cognis); non-ionic surfactant nonyl phenol polyglycol ether ethoxylated with 23 mols ethylene oxide (Ultrawet 23O from Oxiteno S.A.); protective colloid polyvinyl alcohol (Ghosenol GL 05 from Nippon Ghosei China). Tert-butyl hydroperoxide 70 wt.% solution in water (Trigonox A-W70) and sodium formaldehydesulphoxylate (Cosmolit) were used as initiators and supplied by AKZO-NOBEL and Cosmoquímica S.A., respectively.

Sodium bicarbonate as buffer and hydroquinone as inhibitor to quench the polymerization were supplied by MERCK. Lauryl mercaptan used as chain transfer agent was supplied by Phillips.

Deionized water was used in all experiments, sampling procedures and analysis.

The CMC at 25°C were 0.34 and 0.40 g/L for the non-ionic and ionic surfactants, respectively, and were estimated according to literature correlations[13a,b].

The basic polymerization recipe for 65 wt.% total solid contents is shown in Table 1.

Polymerization process

Emulsion copolymerization experiments were carried out in a 1000 mL jacketed glass reactor equipped with a condenser, nitrogen purge line and mechanical agitator. One stream consisting of co-monomers pre-emulsion and two streams of 4.6 wt.% initiators aqueous solutions were fed into the reactor using a diaphragm pump and double head peristaltic pump, respectively. The reaction mixture was controlled to within ±0.5°C with the aid of two constant temperature baths (a low and high water temperature reservoirs) and a control system with a temperature sensor in the reactor.

The reactor was equipped with a four-blade simple paddle impeller. The agitation rate was set equal to 100 rpm to provide adequate mixing and minimize coagulum formation. The pre-emulsion fed to the reactor stood on an electronic balance plate and was adjusted according to the weight indicated. The experimental procedure consisted of initial feed of the reagents to the reactor as shown in Table 1. This initial charge was then purged with nitrogen for 1 h and heated to 74°C. The experiment started with the pre-emulsion and initiators feed, when, simultaneously the reactor temperature set-point was increased to 90°C. The feeding times were of 1, 2, 3, 4 and 6 h. The initiator solutions were fed with a fixed weight relation to the pre-emulsion and proceeded for 30 min, after the end of pre-emulsion feed. The

Table 1 — Basic polymerization recipe (65 wt.% total solid contents)

Reactor initial charge	
Reagent	Mass (g)
Water	120.6
Ultrawet 23O	16.1
Disponil 25 S	3.14
Ghosenol GL 05	1.34
Sodium bicarbonate	2.35
Pre-emulsion	
Vinyl acetate	375.8
Butyl acrylate	93.9
Ultrawet 23O	3.36
Disponil 25 S	0.66
Water	75.8
Lauryl mercaptan	0.91
Initiators	
Cosmolit (aqueous solution 4.6 wt.%)	33.8
Trigonox A-W70 (aqueous solution 4.6 wt.%)	33.8

reaction proceeded further for 30 min, after the end of initiators feed, in order to reach high conversions.

Due to the co-monomers reflux in the condenser the reactor temperature did not rise quickly to the fixed set-point of 90°C. It was observed that after a small temperature jump to 80-82°C, in the first 5 min, it lowered to 76-78°C. From this point onwards the temperature rose slowly to 90°C just after the end of the pre-emulsion feed. Similar temperature profiles in the reactor were observed in all experiments.

Analytical methods

The total solid content was determined gravimetrically at 90°C with a drying time of 12 h. Latex samples of about 1 g were withdrawn from the reactor in 5 to 10 min, intervals and mixed immediately with 0.4 g of a 1 wt.% aqueous hydroquinone solution. The polymer fraction in the samples were determined deducting from the total solid contents, the fraction of non-polymerizable solids (surfactants, protective colloid, sodium bicarbonate, initiators and chain transfer agent), fed to the reactor up to instant *t* of the respective sampling.

The PSD was determined by photon correlation spectroscopy (PCS) with the Coulter N4 Plus. This instrument covered a size range from 30 to 3000 nm and was equipped with a 100 mW He-Ne laser lamp at 632.8 nm and 80 channel digital correlator. The latex samples of 1.0 g were collected in 5 mL glass flasks already containing 2 mL deionized water, 0.05 mL 1 wt.% hydroquinone solution and 0.5 mL 10 wt.% surfactant solution. From these flasks 0.01 mL

samples were then diluted in 3 mL polystyrene tubes containing deionized water. With this water dilution the polymer particles lost residual co-monomers and the analysis determined the particle size distribution of the unswollen particles.

The error in the experimentally measured values of overall conversion and average particle diameter was less than ±5%. The viscosity of the latexes was determined in a Brookfield RVDV-III viscometer with SC4-21 spindle at 20°C. The residual co-monomers were determined by gas chromatography with a Shimadzu HSS-4A head space chromatograph. 30 mg samples were collected over 2 g deionized water, already containing 0.1 g of 1 wt.% aqueous hydroquinone solutions, in a glass flask, which was sealed after sampling.

The amount of dispersed coagulum was determined gravimetrically by sieving 100 g samples diluted to 500 g with deionized water through 40, 80 and 200 mesh sieve plates. The sieve plates containing coagulum water were then dried at 105°C for 2 h. There were no significant co-monomer amounts in the coagulum since the observed overall conversions in the end of each copolymerization run were always higher than 99%.

Results and Discussion

Effect of feeding time on process kinetics

Figure 1 presents, the results of polymerization rate, R_p (g/min), as a function of reaction relative time, t_R, where t is the current process time and t_A is the time at which the addition of the co-monomers was completed. Relative times greater than one mean that polymerization proceeded in batch.

Figure 1 shows that the reaction proceeded under the monomer-starved condition for all the feeding times studied. Figure 3 also shows that the period of the reaction under monomer-starved condition enlarged as the feeding time increased. It is interesting to note that even for the shortest feeding time the monomer-starved condition was observed, although for a short period of the time reaction. This was a consequence of the high propagation rate constant of the co-monomer mixture. For longer feeding times the propagation rate reached quickly the co-monomer addition rates and the monomer-starved condition period enlarged.

Figures 2 and 3 present the effect of the co-monomer feeding times on the time evolution of the instantaneous and overall conversion. The overall
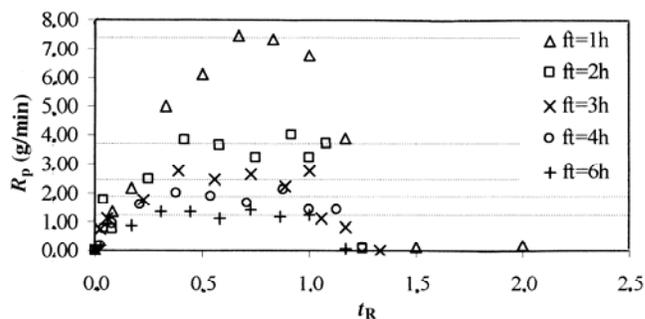

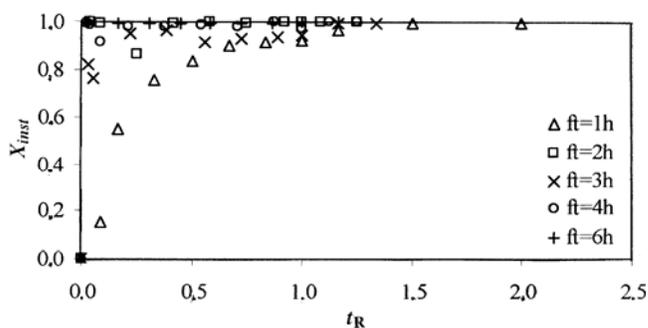Fig. 1 — Effect of co-monomer feeding time, ft, on the polymerization rate, R_p.

Fig. 2 — Effect of co-monomer feeding time, ft, on the instantaneous conversion, X_{inst}.
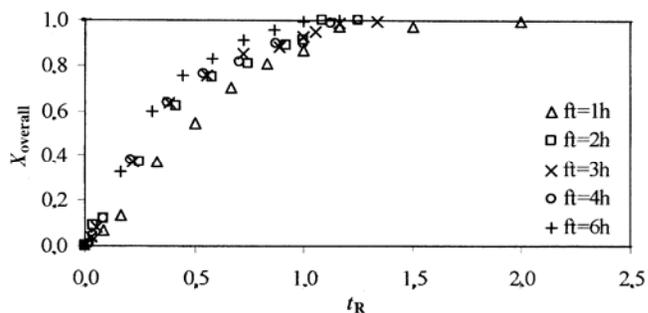

Fig. 3 — Effect of co-monomer feeding time, ft, on the overall conversion, $X_{overall}$.

conversion is defined as the weight ratio between the amount of polymer formed in a given time and the total amount of co-monomers in the standard recipe discounted the co-monomer losses. The instantaneous conversion was defined as the weight fraction of the co-monomers fed and kept into the reactor and the total amount of copolymer produced at that instant.

Figure 2 shows the results of instantaneous conversions determined by the analysis of residual co-monomers in the reactor during the reaction. It is observed that the instantaneous conversion increased rapidly with the feeding time, and all of them are unity for feeding times greater than 3 h. It means that the polymerization rate equals the co-monomer

addition rate and that the co-monomer diffusion rates in the aqueous phase were extremely high and also that the emulsified co-monomer droplets were quickly destroyed in the reactor.

It can be inferred from Fig. 2 that the copolymer composition will be more homogeneous for feeding times greater than 3 h. For feeding times greater than 3 h the copolymer composition will be rather influenced by the feeding time. Figure 3 shows almost complete co-monomer conversion for any feeding time. Similar to the results of instantaneous conversion, (Fig. 2), it is also observed that the overall conversion increased with feeding time.

Figures 4 and 5 present the effect of the co-monomer feeding time on the time evolution of average particle diameter, D_P, and polymer particle concentration, N_P.

Figure 4 shows that the average particle diameter increased with feeding time from 1 to 3 h; for 3, 4 and 6 h the final average diameters are very similar. It was noteworthy that the observed large average particle diameters, was consequence of small quantities of salts in the recipe (initiator, ionic surfactants and buffer). The tested recipe originated from a previous work that had the objective of obtaining high solid content emulsions. The present work complemented the previous one on high solid content emulsions.

The low average diameters observed for feeding time of 1 h had no influence on the VAc monomer loss. The losses were about 10 wt.%, that would represent only 3 vol.% gain in the average diameters, while the final average diameter, shown in Fig. 4, was of 400 nm and 800 nm for feeding times of 1 and 6 h, respectively. It is believed that the final small average diameter for low feeding times was a consequence of the higher concentration of initiator and surfactants in the reactor, leading to enhanced new particles nucleation rate, both, in the aqueous phase and in the particles. Presumably, particles coagulation also occurred, but at a limited rate. For longer feeding times the concentration of initiator and surfactants were also lower than that for smaller feeding times, leading to lower nucleation rate and fewer and greater particles.

For intermediate relative time values the observed tendency inversion can be explained in terms of initiation rate and coagulation rate. The initiation and coagulation rates decreased for feeding times of 1 to 3 h and, consequently, the average particle diameter increased. For feeding times greater than 3 h the particle stability is enhanced with the well established monomer-starved condition. The particles were more stable due to the greater concentration of the hydrophobic butyl acrylate on the particle surface. The same discussion was valid to the results of polymer particle concentration, (Fig. 8), due to the relation between the polymer particle concentration and the average particle diameter.

Figure 5 shows clearly that coagulation rate increased with the feeding time.

The kinetic behaviour of the emulsion systems can be defined by the classification proposed by Smith and Ewart[14] based on the average number of radicals per particle. Figure 6 presents the time evolution of the average number of radicals per particle calculated according the approach proposed by Kong et al[9].
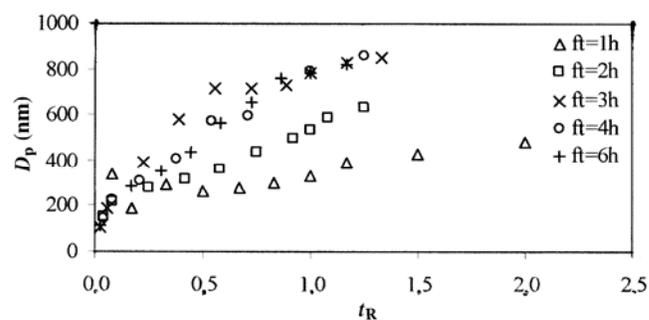

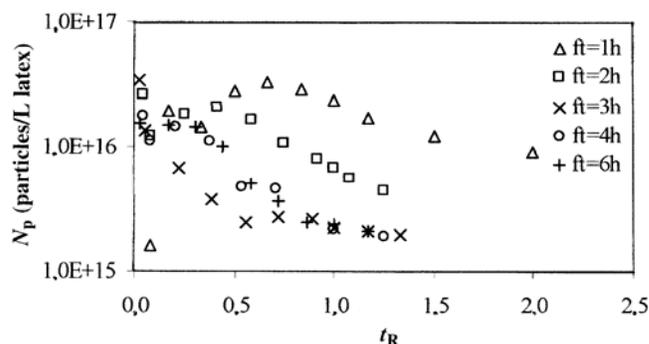Fig. 4 — Effect of co-monomer feeding time, *ft*, on the average particle diameter, D_p.

Fig. 5 — Effect of co-monomer feeding time, *ft*, on the polymer particle concentration, N_p.
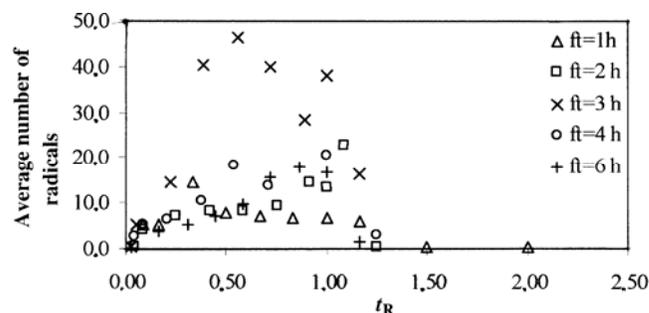

Fig. 6 — Effect of co-monomer feeding time, *ft*, on the average number of radicals per particle.

Figure 6 shows that the average number of radicals per particle was well over 0.5 indicating Smith-Ewart case 3 kinetics for all the feeding times studied, except for the beginning and the end of the reaction. In all the cases, a maximum in the curves was observed. The average number of radicals per particle increased with feeding time from 1 to 3 h and decreased for feeding times of 3 to 6 h. The observed behaviour can be explained in terms of propagation rate, polymer particle concentration, as shown in Figs 3 and 8 respectively, and co-monomer concentration in the polymer particles.

The points of maximum of the curves were consequence of the behaviour of the propagation rate and polymer particle concentration, which also exhibited points of maximum. The observed high values of average number of radical per particle could be consequence of the presence of BuA units in the chains, what obviated the radical transfer events. The lower values of average number of radicals per particle for lower feedings are a consequence of the higher concentration of co-monomer in the particles. The excess of co-monomer in the aqueous phase promoted the swollen of the polymer particle. The higher the co-monomer concentration in the polymer particles the higher the radical transfer to monomer and radical desorption. The tendency inversion was related to the events of particle nucleation and coagulation already discussed to explain the average particle diameter and polymer particle concentration, Figs 4 and 5.

Effect of feeding time on the final properties

Figure 7 presents the effect of the feeding time on the PSD.

Figure 7 shows that, except for feeding time of 2 h, the PSDs were very narrow and similar, considering the displacement of the average particle diameter (Fig. 7). The abnormal result obtained for feeding time of 2 h cannot be appropriately explained with this work and deserves more studies. Figure 7 also shows that particle nucleation and coagulation of the newer formed particles between themselves and to the existing particles occurred along the feeding time.

Figure 8 presents the results of viscosity as a function of the shear rate.

Figure 8 shows that the emulsions behaviour was very similar to that of Newtonian fluids. The viscosity increased with the feeding time of 1 to 3 h, and, as for

the other properties, a tendency of inversion for feeding time of 3 h was also observed. It may be assumed, for a simplified discussion that the main parameters affecting viscosity are the average particle diameter, PSD and total solid contents. The viscosity increased with the feeding time as a consequence of increasing average particle diameter (Fig. 4) and of the overall conversion (Fig. 3). The effect of the PSD (Fig. 7) can be neglected. The slight variation of the viscosity for feeding times greater than 3 h were in accordance with the small variations in the average particle diameter and total solid contents. The abnormal high viscosity for feeding time of 3 h cannot be explained with the observed results of average particle diameter and the total solid contents. Figure 8 also shows, within some experimental error, a limiting viscosity value for feeding times greater than 2 h.

Figure 9 presents the effect of the feeding time on the coagulum formation of the emulsions produced.

Figure 9 shows the formation of a small quantity of coagulum, less than 10^4 ppm, which decreased slightly with feeding time increasing from 1 to 4 h. The coagulum amount increased abruptly to more than 3.10^4 ppm for feeding time of 6 h. The increase can be explained with the longer time available for the particles collision to form coagulum.
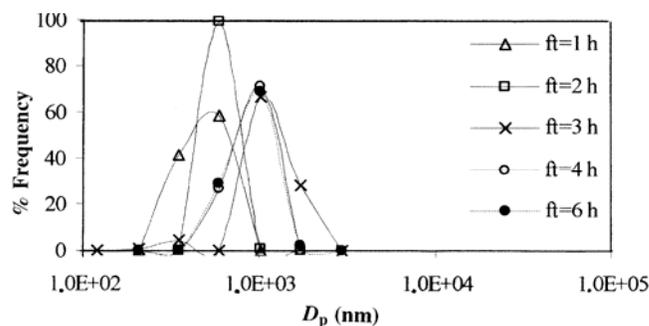

Fig. 7 — Effect of co-monomer feeding time, *ft*, on the particle size distribution.
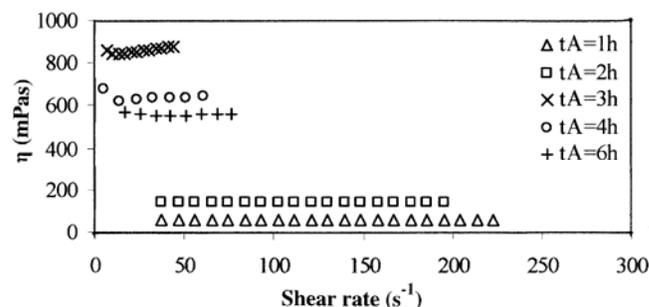

Fig. 8 — Effect of co-monomer feeding time, *ft*, and shear rate on the viscosity, η.
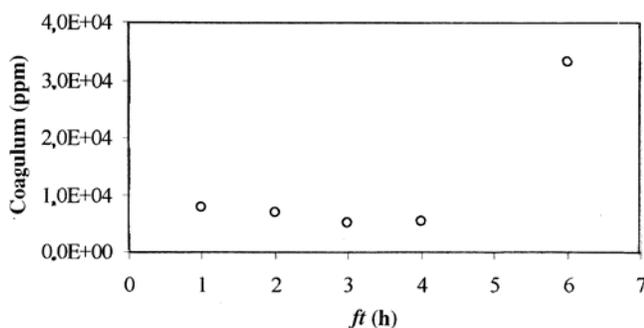
Fig. 9 — Effect of co-monomer feeding time, *ft*, on the amount of coagulum.

Conclusion

The kinetics of a high solid content recipe emulsion copolymerization of vinyl acetate and butyl acrylate was investigated. Effect of feeding time on the variables instantaneous and overall conversion, polymerization rate, average particle diameter, polymer particle concentration, particle size distribution, viscosity and coagulum formation was studied. The particle size distribution was not affected by the feed flow rate, which implies that the semicontinuous process impart intense newer particles nucleation compensated with equally intense coagulation. The process was in the monomer-starved feed condition for the feeding times studied. The polymerization rate decreased with increasing feeding times as a consequence of the higher concentration of initiator, surfactant and co-monomers. The starved condition period enlarged with increasing feeding times. The instantaneous and overall conversion, average particle diameter and polymer particle concentration were affected by the feeding time of 1 to 3 h. For feeding times greater than 3 h the influence was rather small. The lower overall conversions for feeding times shorter than 3 h were due to the loss of VAc. This loss was reduced for feeding times greater than 3 h. The instantaneous and overall conversion increased with feeding time. The monomer-starved condition was always possible due to the high polymerization rate and high co-monomers diffusion rate in the aqueous phase. The average particle diameter increased with the feeding time, while the polymer particle concentration decreased, as a consequence of the decreasing newer particles nucleation rate and also to coagulation. For feeding times greater than 3 h the particle stability was enhanced with the well established monomer-starved condition. The particles were more stable due to the greater concentration of the hydrophobic butyl acrylate on the particle surface. A tendency inversion of the average number of radicals per particle and viscosity was observed. The average number of radicals increased with feeding times of 1 to 3 h and then decreased. The average number of radicals was well over 0.5 indicating Smith-Ewart case 3. This may be due to the presence of BuA units in the chains, that obviate the radical transfer events. The behaviour of the average number of radicals is coupled with the behaviour of the propagation rate and polymer particle concentration. The lower values of average number of radicals for lower feeding times was a consequence of the higher concentration of co-monomer in the particles, higher radical transfer to co-monomer and higher desorption rates. The viscosity increased with feeding time due to the increasing average particle diameter and overall conversion. For feeding times of 4 and 6 h the small variations in the viscosity was related to the small variations of the average particle diameter and overall conversion. The effect of feeding time on the coagulum formation was rather small for feeding times of 1 to 4 h and increased drastically for feeding time of 6 h. The coagulum formation increased with the feeding time due to the longer time available for the particles collision.

Acknowledgements

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