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High Solids Polymer Dispersions

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SUMMARY: High solids polymer latices up to 70% solids content have been prepared by conventional emulsion polymerization from different monomer systems. Emulsifier but also poly(vinylalcohol) stabilization was used. Polymerization process was executed as a two step seeded but also as a single step process. When using known concepts for the control of viscosity for high solids, a high shear viscosity below 50 mPas was achieved even for 70% solids. Quantitative mathematical evaluation of the viscosity depending on bimodal particle size distribution and on the hydrodynamic particle surface layer was possible.

Introduction

High solids polymer dispersions are of increasing interest not only for research but also for new industrial applications. During the last decade a couple of patents appeared (1) and a few new products were offered to the markets, as well as for conventional aqueous adhesives and for pressure sensitive adhesives. Solids content up to 70% and even more(2) can be achieved. Improved application properties(2) but also cost reduction are the dominant driving forces for these trends.

The main issue for the creation of high solids latices is the control of the viscosity when one raises the solids content (sc) up to 60 or 70% or even higher. The basic concept how to control viscosity by particle size distribution (PSD) was developed already 30 years ago: Farris(3) published a semi-empirical quantitative approach to evaluate the viscosity – concentration – relationship for bi-modal or multi-modal PSD's. Surprisingly his concept has not found so much attention. Recently we have shown that the Farris-concept is well applicable within certain limits(4). His approach is used also in this work. For the production of high solids latices one first needs a basic understanding of the main factors influencing the viscosity, second the "know how" for the creation of a desired PSD for a given monomer and stabilizer system and finally, the resulting product should possess required defined application properties.

This contribution is a short summary of some of our work on high solids latices. We studied the emulsion polymerization for emulsifier stabilized acrylic emulsions as well as for the two-

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step (seeded) and for the one-step process. Further, pressure polymerization of vinyl acetate / ethylen (VAE) were executed in the presence of poly(vinyl alcohol), PVOH, as protective colloid. As it is well known that the thickness of the stabilizing particle surface layer δ plays a dominant role for the control of viscosity, we developed a new approach for the quantitative estimation of the δ - value for PVOH stabilized latices[4)].

”Two-Step” (Seeded) Emulsifier Stabilized Vinyl-Acrylic Latices

Using bimodal seed latices, prepared from a single step emulsion polymerization, we were able to produce final dispersions up to 70% solids content with high shear viscosity below 5000 mPas, depending on PSD as shown in Fig. 1. PSD’s were estimated using a COULTER LS 230 device. It is known that these PSD’s have to be corrected to give the true portions of each fraction. Seed A, which was used to produce the PSD’s in Fig. 1 was a commercial emulsifier stabilized VAE-ethylhexylacrylate latex, containing 8% of functional monomers, such as acrylic acid and arcyl amide. 10 parts of this 60% latex and 10 parts water formed the seed. 30 parts water, 2.5 parts surfactant, 80 parts acrylic monomer, 10 parts vinylester and 3.5 parts functional monomers were fed to this seed as a preemulsion (latex 2 and 3) or separately as an aqueous and monomer feed (latex 1 and 4). Additional emulsifier was added to the seed for latex 1 and 2. Reaction was initiated by K-peroxy-difulfate and Na-formaldehyde- sulfoxylate.

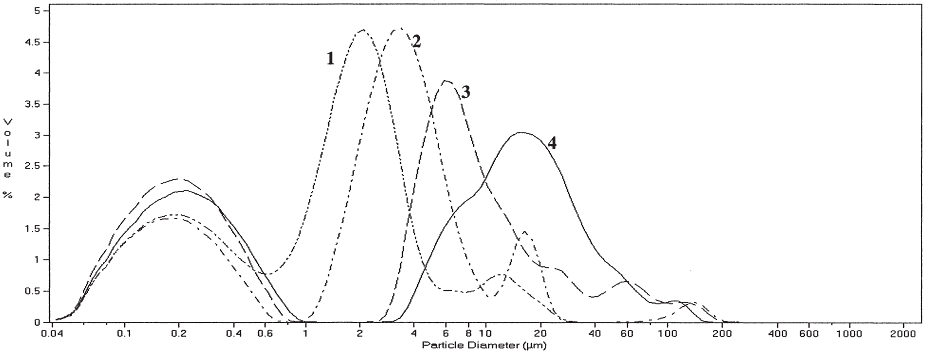

Fig. 1: PSD’s for latices obtained by seeded polymerization of seed A; following solids and high shear viscosity was achieved for the final latices:

latex 1: sc 66.8 %, 11 200 mPas
latex 2: sc 66.7 %, 7 600 mPas
latex 3: sc 68.0 %, 5 850 mPas
latex 4: sc 69.4 %, 3 530 mPas

PSD from Coulter LS 230 shows differential volume distribution versus particle diameter in μm (similar graphs will be given in Figs. 2, 4, 5, 6)

As well known, the PSD's of the final latices can be adjusted by the emulsifier level, chosen for the seed. The feed procedure (preemulsion or separate feed) did also influence the resulting size distribution, surprisingly. The decrease of viscosity is most effective in general if the diameter ratio (small/large) $R_{1,2}$ of the two polydisperse fractions becomes less than $R_{1,2} = 0.1$. Due to the contribution of the particle surface layer, the amount of functional monomers and the electrolyte content played a significant role for the viscosity level, too.

The particle growth of the fractions was not always as one would expect from known "competitive growth" experiments / theory[5)]. When the seed contained larger amounts of functional monomer no growth of the smaller particle fraction was observed. In Fig. 2 the change of PSD is displayed for two different seed latices. Seed A was prepared with 8% functional monomer whereas seed B contained only 4%.

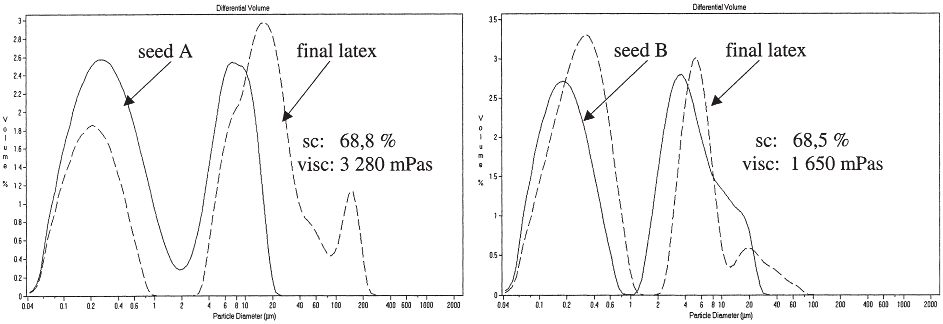

Fig. 2: PSD's for seed and final latices, indicating no growth of the small particles for seed A, containing higher amount of functional monomer.

"One-Step" Emulsifier Stabilized Acrylic Latices

Recently we prepared bimodal acrylic latices, consisting mainly of poly(butyl acrylate), in a single step emulsion polymerization. These dispersions are stabilized by emulsifier and contain 1% acrylic acid. One key role for the control of PSD is the emulsifier level in the reactor during the course of the polymerization. If the mean diameter ratio of the polydisperse fractions is in the range of about 1:10, then viscosity below 50 mPas can be achieved even at 70% solids! This is in sufficient concordance with predictions on the basis of the Farris model[3)]: Within the Farris concept the relative viscosity η_r for a volume concentration Φ may be expressed as:

$$\eta_r(\Phi) = \eta_r(\Phi_1)\eta_r(\Phi_2);\quad \Phi_1 = \frac{V_1}{V_1 + V_{DM}};\quad \Phi_2 = \frac{V_2}{V_1 + V_2 + V_{DM}};\quad \Phi = \Phi_1 + \Phi_2 - \Phi_1\Phi_2$$

For the volume fractions of the small and the large particles, Φ_1 and Φ_2, one obtains:

$$\Phi_1 = \frac{\Phi - (1-f)(1-\varepsilon)\Phi}{1-(1-f)(1-\varepsilon)\Phi}; \quad \Phi_2 = (1-f)(1-\varepsilon)\Phi$$

V_1, V_2, V_{DM} are the volumes of the small and the large particles and of the dispersion medium, respectively, ε is the mass fraction of the small particles and f is a "crowding factor". This "fitting parameter" $0 \leq f \leq 1$ is negligible as long as $R_{1,2} \leq 0.1$[4,6].

For the concentration dependence of viscosity a couple of hundred equations have been published[6]. For hard sphere like behavior the expression $\eta_r(\Phi) = (1 - \Phi/\Phi_M)^{-2}$ is quite useful. $(1 - \Phi/\Phi_M)$ represents the "free volume" for particle motion within a shear field, with Φ_M being the maximum packing fraction, mainly used as a fitting parameter. For monodisperse hard spheres one obtains $\Phi_M \approx 0.60...0.63$ for the low shear limiting viscosity and $\Phi_M \approx 0.69...0.71$ for the high shear limit. With increasing polydispersity Φ_M increases[7], but for a monomodale PSD one never reaches such an increase of the packing fraction as for bimodal or multimodal ones.

Fig. 3 displays the results for model calculations based on the given equations for the low and the high shear limiting viscosity of a 70% latex, varying the thickness of the hydrodynamic surface layer ($\delta = 0\ nm$ and $\delta = 5\ nm$). The huge influence of the particle surface layer is very obvious. The high solids system will only be achievable , if a fraction of the smaller particles between about 15 and 40 % can be produced during the polymerization. As it turns out from such calculations, viscosity below 50 mPas can only be achieved at 70% solids, if the two fractions itself possess a broad PSD, so that their maximum packing fraction is beyond the figures for monodisperse systems.

Figs. 4 and 5 give the experimental results for 70% poly(butylacrylate) latices 1 and 2 for a pH value of 4.5. Comparison of the results shows, that the broader the PSD of the two fractions and the larger their diameter ratio, the smaller is the viscosity. Quantitative PSD's are taken again from COULTER LS 230 measurements.

The well known influence of the pH on viscosity is shown in Fig. 6 for latex 3. Even for the small amount of 1% of acrylic acid used for the polymerization, the increase of pH causes a "swelling" of the particle surface layer[8]. For this third latex a trimodal PSD was obtained. Comparison to the bimodal PSD's for latices 1 and 2 in Figs. 3, 4, the trimodal distribution does not give a lower viscosity. As it follows from theory, the third component would be only effective regarding lowering the viscosity if the particle size of that third component would be again about ten times above the second one. This does not seem to be a realistic solution for practical use.

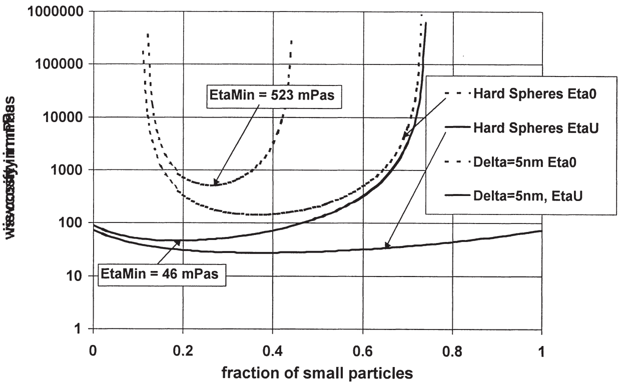

Fig. 3: Viscosity in dependence on the mass fraction of the small particles for a bimodal particle size distribution, for the low shear limit (η_0 = Eta0) and the high shear limit (η_∞ = EtaU), solids content = 70% by mass, particle density = 1.14 gcm^{-3}, maximum packing fraction for the particle fractions: $\Phi_{M,0} = 0.6$, $\Phi_{M,\infty} = 0.76$.

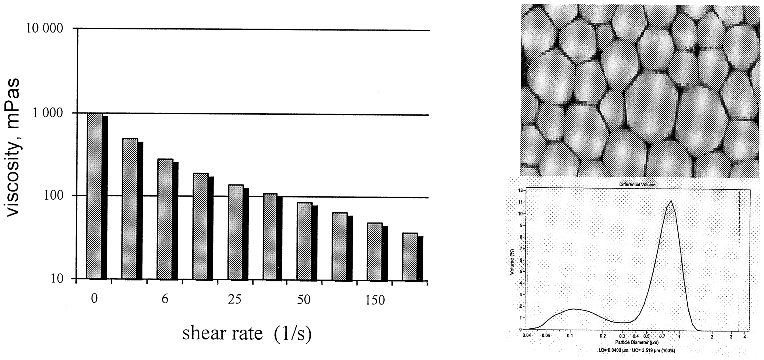

Fig. 4: Viscosity and PSD of the 70% poly(butylacrylate) latex 1

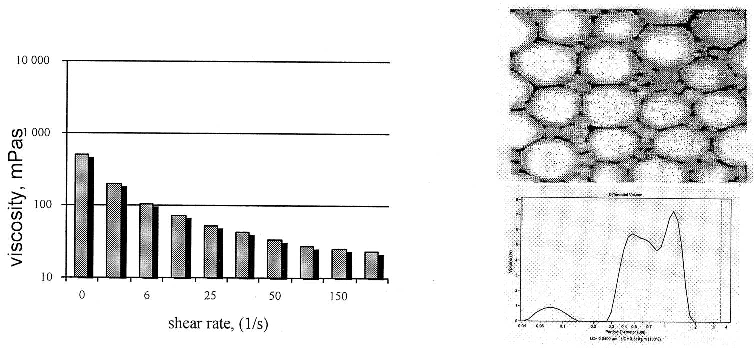

Fig. 5: Viscosity and PSD of the 70% poly(butylacrylate) latex 2

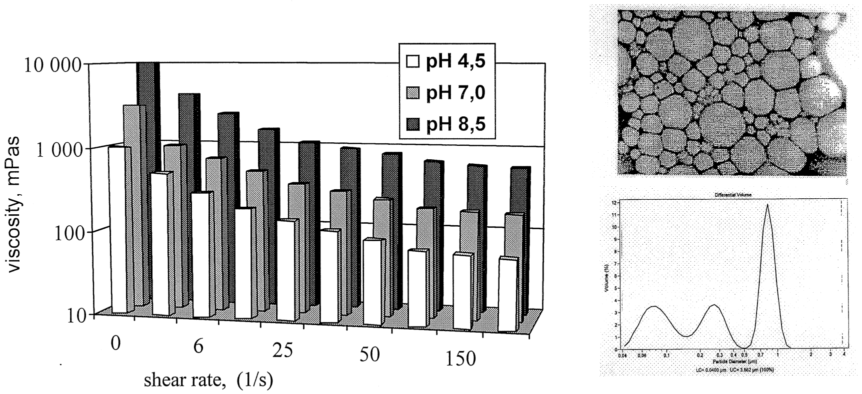

Fig. 6: Influence of pH value on viscosity for the 70% poly(butylacrylate) latex 3, PSD is trimodal

"One-Step" PVOH stabilized VAE Latices

The viscosity of the aqueous phase and the thickness of the PVOH layer, adsorbed or grafted to the particles will be very effective for latices only stabilized by PVOH. Therefor we developed a new approach to detect the thickness of the particle surface layer for such dispersions[4)]. When one estimates the specific viscosity $(\eta_s/\Phi)_{\Phi\to 0}$, there are two contributions: One from the particles with the PVOH-layer δ and the other from the solved part of the PVOH $[\eta]$. Taking into account as well as the adsorbed/grafted PVOH fraction $\alpha' = V^{ads}{}_{PVOH} / V^{total}{}_{PVOH}$ and the ratio of particle / PVOH volume $v = V_{particle} / V^{total}{}_{PVOH}$, one derives the following equation for the δ-value for the monodisperse limit (x_{HS}: hard sphere particle diameter, $k_E = 5/2$),

$$\delta = \frac{x_{HS}}{2}\left[\left(\left(\frac{\eta_s}{\Phi\, k_E}\right)_{\Phi\to 0}\left(\frac{v+1}{v+\alpha'}\right)-\left(\frac{[\eta]}{k_E}\right)\left(\frac{1-\alpha'}{v+\alpha'}\right)\right)^{\frac{1}{3}}-1\right]$$

Depending on the ratio v^{-1} one estimates δ values between 20 nm and 40 nm for a PVOH (Mowiol 04/88) with a molecular weight of about 57000 gMol^{-1} weight average and a saponification of 88%. Only 20-30% of the PVOH were bonded to the particles[4)]. Using this PVOH as a protective colloid for pressure emulsion polymerization of vinylacetate/ethylen with some functional monomer one may obtain high solids latices. Based on the estimated δ-value and on the above given Farris concept, we were able to describe quantitatively the viscosity-concentration-dependence for bimodal PVOH stabilized VAE-latices up to about a solids content of 70 %, compare Fig. 7.

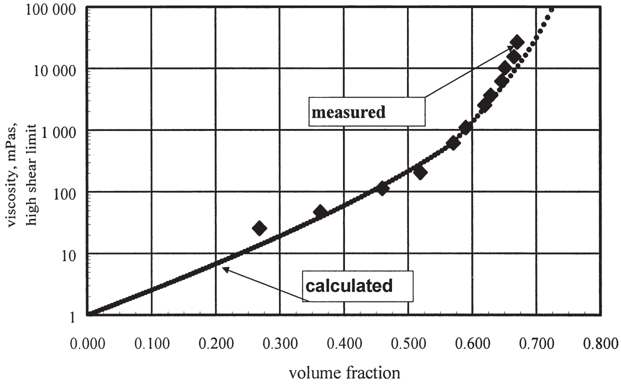

Fig. 7: Viscosity - concentration dependence for a PVOH stabilized VAE latex; calculated line according to the Farris model, calculations took into account: $\Phi_{M,0} = 0.63$ and $\Phi_{M,\infty} = 0.7$, $\varepsilon = 0.65$ and $\delta = 20\,nm$. The change of aqueous phase viscosity with latex concentration was also considered.

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