

Shear Thinning Behavior of Concentrated Latex Dispersions

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Summary: Measured viscosity vs. shear rate relationships were analyzed for a wide variety of carboxylated latexes reported in the literature using the theoretical model proposed by one of the authors. The theory contains three main parameters: c_m , k_o and δ , which are the maximum volume fraction, a particle interaction parameter closely related to the secondary electroviscous effect, and the thickness of the stabilizing surface layer, respectively. It is assumed that sheared dispersions always approach close packing for high volume fractions, *i.e.* $c_m = 0.74$, and that the shear thinning is entirely due to the energy dissipation associated with hydrodynamic and colloidal particle interactions, which at low shear rates is larger than at high ones (for simple shear flows). The experimental data include those by Laun who measured the viscosity of concentrated latex dispersions over nine order of magnitude of shear rate ranging from 10^{-3} to 10^6 s^{-1} , and Chu *et al.*, who prepared several monodisperse latexes and measured the viscosity of individual as well as trimodal blends of these three latexes as a function of shear rate. The viscosity of carboxylated latex is also influenced by surface “hair”, which appears to be closely related to the amount and type of functional monomers, and degree of dissociation of carboxylic acid groups on the latex surface.

Keywords: carboxylated latex; electroviscous effects; polymer dispersions; shear thinning

Introduction

The apparent viscosity of a liquid increases with addition of small colloidal particles. The first person to calculate this increase in viscosity with volume fraction, c , of the colloidal particle was Einstein,^[1,2] who obtained the result, valid for low volume fraction $c \ll 1$:

$$\mu = \mu_o(1 + 2.5c) \quad (1)$$

Here μ is the apparent viscosity of the dispersion and μ_o that of suspending medium. Numerous theoretical and (semi)-empirical expressions have been developed in efforts to extend Einstein's formula to

dispersions of higher concentrations. Among these, the one derived by Krieger and Dougherty^[3,4]

$$\mu = \mu_o \left(1 - \frac{c}{c_m}\right)^{-2.5c_m} \quad (2)$$

is, perhaps, the most widely cited to explain the observed sharp increase in μ at high volume fractions, c , as well as the strong shear thinning behavior. Here, c_m is the critical volume fraction at which the viscosity of the dispersion reaches an infinite value. The magnitude of c_m depends on the packing of the particles in the dispersion. For randomly packed spheres of the same size (for which Brownian motion dominates the distribution of particles) $c_m \cong 0.57$, while for hexagonally close-packed spheres, $c_m \cong 0.74$ at high shear rate, G . Additional parameter(s) are needed to correlate basic surface properties of the latex dispersions to their rheological properties.

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Among many (semi)empirical expressions, the one proposed by van de Ven has one unique feature.^[5] He argues that $c_m = 0.74$, regardless of G , because at high volume fractions, sheared concentrated dispersions are always ordered when steady-state conditions prevail.^[6–10] His expression:

$$\mu = \mu_o \left[\frac{1 - c/c_m}{1 - (k_o c_m) c / c_m} \right]^{\frac{-2.5 c_m}{2 - k_o c_m}} \quad (3)$$

contains one additional particle interaction parameter related to the hydrodynamic forces, k_o , assuming that the shear thinning is a result of the energy dissipation associated with hydrodynamic and colloidal particle interactions, which at low shear rate is larger than at high ones (for simple shear flow). Through rigorous hydrodynamic analysis, he predicted that $k_o \cong 1.7$ at the high-shear limit.

The low shear limit of k_o is, however, expected to be influenced by various colloidal forces acting on particle including an increase in viscosity due to the presence of electrical double layers around the colloidal particles, and the electrostatic and electrosteric interactions among highly

charged colloidal particles (primary and secondary electroviscous effects). The exact function of k_o vs. G highly depends on surface properties of latexes, as well as the electrolyte concentration in the aqueous phase of the dispersion.

Analysis of Experimental Data

Laun has reported one of the most comprehensive measurements of the viscosity of concentrated latex dispersions as a function of G .^[8,11] His results for styrene-ethylacrylate, ST-ET, latex are reproduced in Figure 1 by solids symbols. This latex was synthesized with 3% acrylic acid and 2% maleic acid in the presence of 0.5% of a sulfonate-type anionic surfactant (Here and subsequently all concentrations of functional monomers and added surfactants are expressed as a percentage relative to the concentration of the main monomers.). $K_2S_2O_8$ was used as the initiator, and the latex was freeze-dried to obtain a dried-powder. It was then redispersed into aqueous NaOH solutions to prepare dispersions at desired particle volume fraction and $6.2 < \text{pH} < 6.5$. The

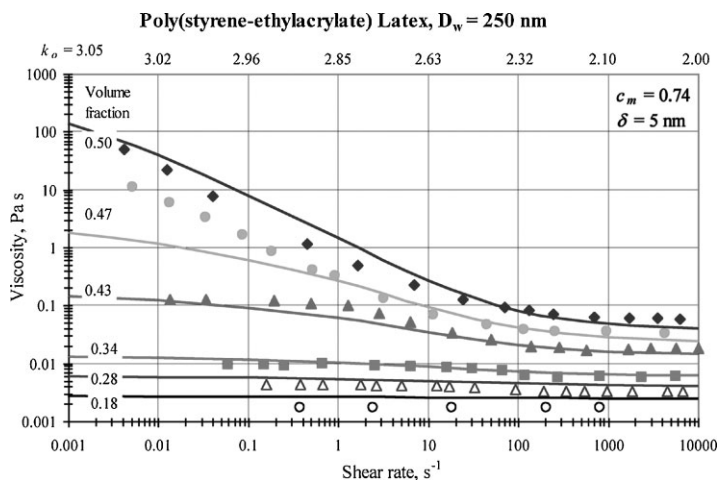


Figure 1.

The viscosity vs. shear rate relationships of styrene-ethylacrylate latex of $\text{pH} = 6.2\text{--}6.5$ at the volume fraction ranging from 0.18 to 0.50, measured at 25°C .^[11] Solid lines are the predicted relationship from Eq. (3) using k_o -values shown at the second x-axis on top, which successfully explains the measured μ at $10^{-3} < G < 10^4$, except that at the volume fraction $c = 0.47$ at $G < 0.1\text{ s}^{-1}$.

redispersed latex had a diameter of $D_w = 250$ nm with $D_w/D_n = 1.04$, where D_w and D_n are the weight and number average particle diameter, respectively, as measured by the analytical ultracentrifuge. The Na^+ concentration in the latex varied with volume fraction from 0.09 to 0.23 M for dispersions at $c = 0.28$ –0.50.

A series of solid lines in the figure illustrates predicted μ vs. G for c -values ranging from 0.18 to 0.50 and $10^{-3} < G < 10^4$ using $c_m = 0.74$, $\mu_o = 1$ mPa · s and $\delta = 5$ nm, where δ is the thickness of the polycarboxylic acid „hairy” layer on the latex surface. Here, c in Eq. (3) was replaced by an „effective” volume fraction: $c_{\text{eff}} = c(1 + \delta/a)^3$, where a is the particle radius. The measured μ -values shown in Figure 1 span nearly five orders of magnitude from 10^{-3} to just below 10^2 Pa · s, and Eq. (3) adequately fits all measured μ vs. G except that for $c = 0.47$ at $G < 10^{-1} \text{ s}^{-1}$. It is especially significant that a single value of $\delta = 5$ nm can be used for the entire range of c and G examined. This is quite in contrast to a similar analysis by Chu *et al.*, using Eq. (2).^[12] They needed to vary δ -values from 3.7 to 10 nm depending on c and a , even though their analysis was limited to

μ -values at the low-shear Newtonian plateau.

By assuming k_o is only a function of Péclet number; $Pe = Ga^2/D$, where D is the diffusion constant, and for the spherical particles, $D = k_B T / 6\pi\mu_o a$, k_B is the Boltzmann constant and T the absolute temperature, the k_o vs. Pe relationship, shown in Figure 2 by solid circles, is successfully fitted by the relation:

$$k_o = k_o^\infty + \frac{(k_o^0 - k_o^\infty)}{1 + Pe^{0.35}} \quad (4)$$

Here, $k_o^\infty = 1.70$ and $k_o^0 = 3.05$ are the high and low shear limits of k_o , respectively. Besides replacing c in Eq. (3) by c_{eff} (and c_m by c_m^{eff}), the value of δ also modifies the Péclet number, as a must be replaced by $a + \delta$.

Laun has also reported μ vs. G for a commercial styrene-butylacrylate latex at 50% solids.^[11] The μ vs. G were measured at two different pH's of 4.5 and 7.7, as illustrated in Figure 3. As seen, Eq. (3) with Eq. (4) adequately fits the measured μ vs. G at pH = 4.7 using $\delta = 2$ nm with $\mu_o = 1$ mPa · s. A higher dissociation of carboxylic groups on the latex surface should result in an extended „hairiness”, which causes an increase in δ , thus in a higher μ .

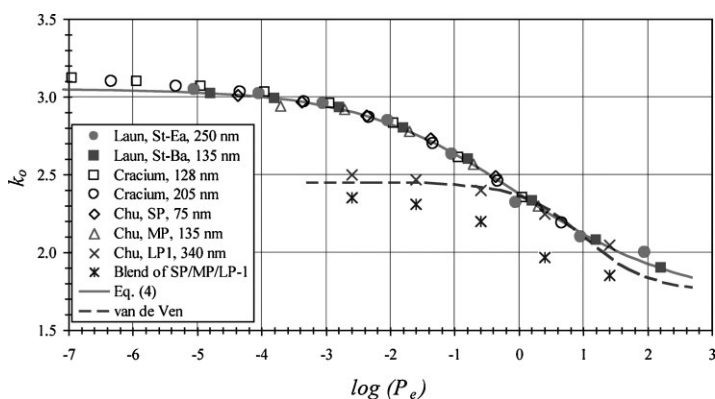


Figure 2.

The k_o -values used to best fit the measured μ vs. G relationships shown in Figure 1 are plotted against Pe (solid circles), and successfully fitted by Eq. (4) using variables shown in the text. The k_o vs. Pe relationships used to fit measured data for the other 7 carboxylated latexes (soft spheres) shown in Figure 3 to 6 are also included. All those k_o vs. Pe are in good agreement with those predicted from Eq. (4) except Latex LP-1 and blend of three latexes by Chu *et al.*^[12] The dashed line represents the predicted relationship by van de Ven^[5] through the analysis of measured data of dispersions of hard spheres by Papir and Krieger.^[13]

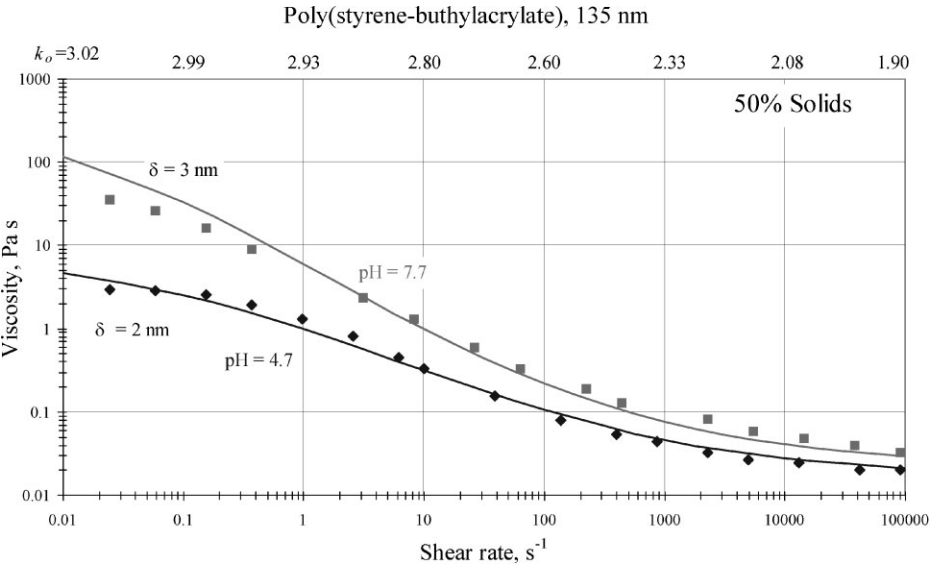


Figure 3. The measured μ vs. G relationships of styrene-buthylacrylate latex at 50% solids by Laun.^[n] Eq. (3) with k_o from Eq. (4) successfully fits the measured relationships by simply increasing $\delta = 2$ nm to 3 nm when the latex pH is increased from 4.7 to 7.7. The k_o values used are indicated at the second x-axis on top.

The measured μ vs. G at pH=7.7 is expected to be fitted by simply increasing the thickness of the hairy layer, but keeping the same k_o vs. Pe relationship. This is indeed the case, as seen in Figure 3, by upper solid line using $\delta=3$ nm. No other adjustments were made for variables in Eq. (3). Including keeping $c_m=0.74$ throughout the analysis.

Cracium *et al.*, report the measured μ vs. G relationships of two surfactant-free carboxylated styrene-butadiene latexes of $D_w=128$ and 205 nm identified as Latex 1 and Latex 2, respectively.^[14] These latexes are synthesized with 4 and 2% acrylic acid, as shown in Table 1, to have comparable carboxylic acid groups of 7.5×10^{18} and

$6.0 \times 10^{18} \text{ m}^{-2}$ for Latex 1 and Latex 2, respectively. It is known that the acrylic acid forms highly water soluble oligomeric materials during the emulsion polymerization, resulting in only $\sim 50\%$ of these being grafted on the latex surface.^[15] Since 2×10^{18} carboxylic acid groups m^{-2} are required for monolayer coverage of latex, these latexes have enough surface groups to provide the electrostatic and electrosteric interactions, required for stability.^[16]

The measurements were conducted at $10^{-4} < G < 10^3 \text{ s}^{-1}$ and 55 weight % solids, which corresponds to $c=0.525$ because of the polymer density is 1.05. Results of measured μ vs. G are illustrated in Figure 4 by solid symbols for these

Table 1. Chemical composition and physico-chemical properties of two styrene-butadiene latexes used by Cracium *et al.*^[14]

	% Styrene	% Butadiene	% Acrylic acid	Diam., nm	Zeta Potential, mV	pH	Total surface area per 100g dry latex, m^2	Acrylic acid per m^2
Latex 1	88	8	4	128	-41^*	2.5	4.5×10^3	7.5×10^{18}
Latex 2	89	9	2	205	-47^*	8.0	2.8×10^3	6.0×10^{18}

*Measured for a dilute suspension ($\sim 0.1\%$), at $l=0.001$ M.

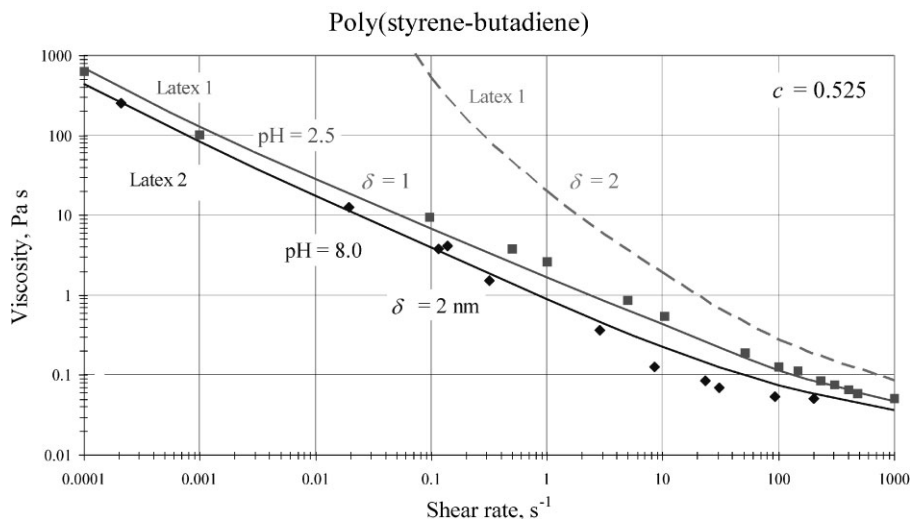


Figure 4.

Same as Figure 3 but for Latex 1 of 128 nm and Latex 2 of 205 nm by Cracium *et al.*^[14] Eq. (3) and (4) (solid lines) fit measured data (symbols) of two latexes and pH-values by just using a larger δ -value at the higher pH. Slightly larger than predicted k_o -values, shown in Figure 2, are used at $G < 1 \text{ s}^{-1}$ to fit the measured relationships better. The dashed line is the predicted μ vs. G for Latex 1 at pH = 8 ($\delta = 2 \text{ nm}$).

latexes and successfully fitted by Eq. (3) and (4), as shown by solid lines, using $\delta = 1$ and 2 nm for these measured at pH = 2.5 and 8.0, respectively, together with $\mu_o = 1.0 \text{ mPa} \cdot \text{s}$ and $c_m = 0.74$. It is especially significant that Latex 2 is roughly twice as large as Latex 1, but Eq. (4) successfully predicts the k_o vs. Pe relationships for both latexes. Slightly higher k_o -values, as shown by solids diamond and triangle symbols in Figure 2, are used to fit the measured results better at $G < 1 \text{ s}^{-1}$. The predicted values of Latex 1 at pH = 8 are also shown in Figure 4, indicating that the viscosity can increase tremendously by simply increasing the thickness of the hairy layer from 1 to 2 nm.

Chu *et al.*, have reported detailed measurement of μ vs. G of three styrene-butylacrylate latexes identified as SP, MP and LP-1, respectively.^[12] Even though NaOH is listed in the ingredients used, the pH of these latex dispersions is not specified in the paper. They measured μ vs. G of these latexes at a wide range of c as shown in Figure 5 and 6.

The smallest size, Latex SP, is polymerized with only 0.2% of methacrylic acid,

MAA, and contains a total of 9.5% of polyoxyethylene-based anionic and non-ionic surfactants. This high level of surfactant should increase μ_o - and δ -values, as the adsorbed surfactants on the latex surface extend their polyoxyethylene chains toward the bulk water. As seen in Figure 5a, measured μ vs. G relationships for this latex were successfully fitted by Eq. (3) with Eq. (4) assuming $\mu_o = 1.5 \text{ mPa} \cdot \text{s}$ and $\delta = 2 \text{ nm}$ for all c studied except that at $c = 0.443$.

The latex MP of $D_w = 135 \text{ nm}$ is synthesized with a total of 4.7% of non-ionic and anionic surfactants with 1.0% MAA. The measured μ vs. G are again successfully fitted by Eq. (3) and Eq. (4) together with $\mu_o = 1.3 \text{ mPa} \cdot \text{s}$ and $\delta = 1 \text{ nm}$, as shown in Figure 5b. Here, k_o -values at $G = 0.1 \text{ s}^{-1}$ had to be lowered slightly from the predicted value of 2.99 to 2.94 to fit the measured relationship better. The predicted μ -values for the highest $c = 0.567$ still significantly deviated from measured values at $G < 1 \text{ s}^{-1}$. The open diamond and triangle symbols in Figure 2 represent k_o -values used for Latex SP and MP, respectively.

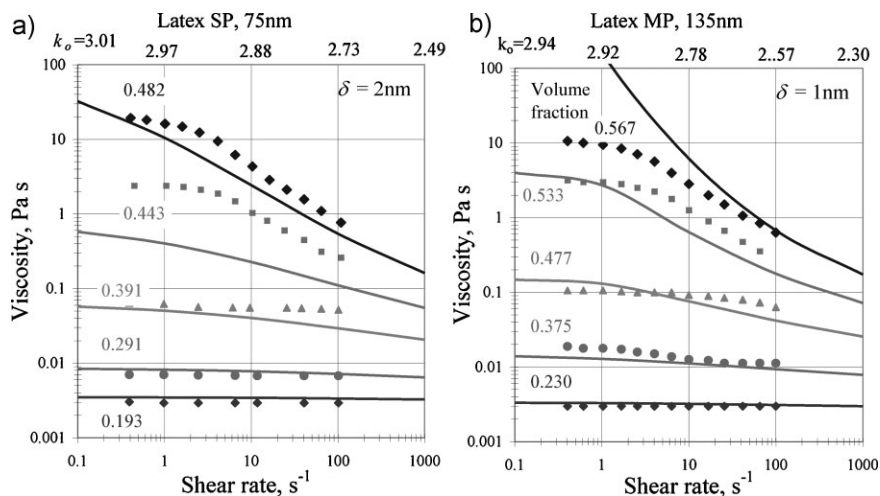


Figure 5.

Measured μ vs. G of Latex SP and MP by Chu *et al.*^[12] Lines indicate the predicted relationship by Eq. (3) and Eq. (4), which fit adequately for Latex SP at the entire shear rate range measured except that for $c = 0.443$. When Eq. (4) overestimates measured μ for Latex MP at $G < 1 s^{-1}$ using the k_o -values predicted by Eq. (4), slightly lower k_o -values are used to fit the measured relationship better.

The largest size, Latex LP-1 of 340 nm in diameter is synthesized with 1.5% of MAA and a total of 2.45% of polyoxyethylene surfactants. Eq. (3) with Eq. (4) explains the measured relationships adequately only at $G = 100 s^{-1}$ with $\delta = 1 nm$ and $\mu_o = 1.1 mPa \cdot s$, but significantly lower than pre-

dicted k_o -values are needed at lower shear rate (see Figure 6a). The cross symbols in Figure 2 represent the k_o vs. Pe relationship used to best fit the measured μ vs. G relationships for Latex LP-1. It is of particular interest that the dashed line in the figure represents the original k_o vs. Pe

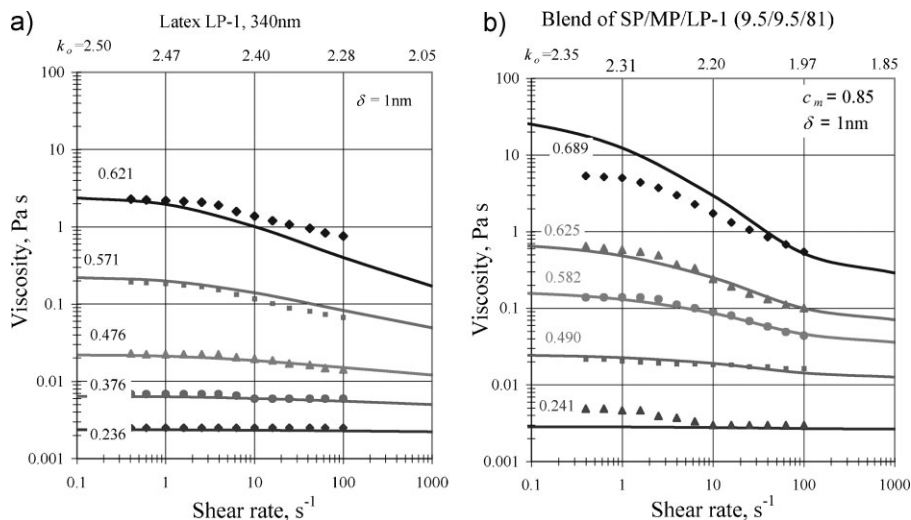


Figure 6.

Same as Figure 5 but for Latex LP-1 and 9.5/9.5/81 blend of Latex SP, MP and LP-1 by Chu *et al.*^[12] The k_o -values have to be systematically lowered for Latex LP-1 and SP/MP/LP-1 (crosses and stars in Figure 2) from those predicted by Eq. (4) even at $G = 100 s^{-1}$, because electroviscous effects are weaker.

established by van de Ven^[5] to fit the measured data reported by Papir and Krieger.^[13] The relationship by van de Ven can be expressed similar as Eq. (3) with slightly different variables as:

$$k_o = k_o^\infty + \frac{(k_o^0 - k_o^\infty)}{1 + 0.1Pe^{0.35}} \quad (5)$$

with $k_o^0 = 2.46$.

The paper by Chu *et al.*, also includes measured μ vs. G for a blend of the three latexes SP, MP and LP-1 at 9.5/9.5/81 ratio (Figure 6b). These data are first fitted with the same k_o vs. Pe and all other variables as Latex LP-1, by simply increasing c_m from 0.74 to 0.85 to represent the broad size distribution. The predicted μ -values from Eq. (3) were consistently above the measured ones except these at the lowest c of 0.241. For example, the predicted μ -values is nearly 4× of the measured value of μ at $G = 10 \text{ s}^{-1}$ and $c = 0.625$. Further increase in c_m did not improve the fit. The predicted μ vs. G from Eq. (3) fits better when k_o -values are further lowered over the entire range of shear rates studied, as shown by the solid lines. It is no surprise that lower k_o -values are needed to fit the blend of these unequal-size spheres. The minimum separation distance of two colliding spheres in simple shear flow is a strong function of their size ratio and sharply increases as one sphere is smaller than the other.^[17]

All k_o vs. Pe relationships for Chu *et al.*, Cracium *et al.*, as well as Laun's data are included in Figure 2, which demonstrates that the mathematical relationship developed by van de Ven shown in Eq. (3) together with the unified k_o vs. Pe relationship of Eq. (4) adequately explains measured μ vs. G of a total of six concentrated latex dispersions, their particle size ranging from 75 nm to 250 nm at $0.002 < \mu < 60 \text{ Pa} \cdot \text{s}$ and $10^{-3} < G < 10^4 \text{ s}^{-1}$. It is also significant that the δ -value appears to be closely related to latex surface properties, such as the thickness („hair” length) of the dissociated carboxyl groups and/or the adsorbed surfactant layer on the latex surface. The observed deviation of k_o -values, with two other latexes, from that

predicted by Eq. (4) at low shear rate is likely related to a different magnitude of the secondary electroviscous effect, and the chemical composition and thickness of the surface layer; both the magnitude of the secondary electroviscous effect and the thickness of the surface layer depend on the electrolyte concentration in the aqueous phase of the latex dispersion.

Discussion

We, here, provide strong evidences that equation (3) by van de Ven^[5] successfully predicts the measured viscosity of concentrated latex dispersions over a wide range of conditions of $10^{-3} < \mu < 10^2 \text{ Pa} \cdot \text{s}$ and $10^{-3} < G < 10^4 \text{ s}^{-1}$ using the k_o vs. Pe relationship predicted by Eq. (4) with $c_m = 0.74$, the value for hexagonal close packing of monodisperse dispersions. In this equation, the shear thinning is entirely due to the shear dependence of k_o , a result of the energy dissipation associated with hydrodynamic and colloidal particle interactions, which at low shear rates is larger than at high ones. This is in contrast to a similar relationship, Eq. (2), proposed by Krieger-Dougherty,^[3] where the shear thinning is the result of changes in c_m from 0.57 for randomly packed spheres at $Pe \ll 1$ to 0.74 at $Pe \gg 1$. The „hair” length δ used to estimate the „effective” volume fraction in Eq. (3) appears to be the function of the surface property of the latex particle, and thus can be correlated with the type and degree of grafted or adsorbed surface groups (*i.e.* carboxylation), pH of the latex dispersion and the presence/absence of surfactants, especially those with long polyoxyethylene chains.

The k_o vs. Pe relationship given by Eq. (4) fits measured μ vs. G relationships for 6 out of 8 latexes tested in this study without modification at $10^{-7} < Pe < 10^2$ with $k_o^0 = 3.05$ (see Figure 2). These 6 latexes cover diameters ranging from 75 nm to 250 nm, and chemical composition from polyacrylates to poly(styrene-butadiene), all of them prepared in the presence of

acrylic, methacrylic and/or maleic acid(s). The carboxylic acid level of these latexes varies widely from 0.2% methacrylic acid (Latex SP by Chu *et al.*) to 3% acrylic acid plus 2% maleic acid (ST-ET latex by Laun), and a total surfactants level of 0.5%–9.5%. These latexes are stabilized through electrostatic repulsive forces and short range electrosteric interactions due to grafted or adsorbed surface layers. Therefore, these latexes are considered to behave as soft spheres with strong interparticle colloidal forces which result in a significant secondary electroviscous effect.

The secondary electroviscous effect is a strong function of the electrolyte level in the latex and ζ -potential.^[5,18] The ζ -potential is highly influenced by the ionic strength and the location of the shear plane, but only weakly related to the surface charge density^[16,19] and/or chemical composition of the „hairy” surface layer. Laun reports that the ζ -potential of his ST-EA latex show only a minor change from –35 to –39 mV when the latex pH is increased from 3.7 to 9, respectively. The measured μ , however, increased nearly 25× from ~0.13 to above 3 Pa·s at $c \sim 0.48$ and $G = 0.1 \text{ s}^{-1}$ as the latex pH increased from 5.1 to 7.0^[8] presumably due to an increase in δ from less than 3 nm to nearly 6 nm. The ionic strength for the ζ -potential measurement is not specified in the paper.

Latex 1 and 2 by Cracium *et al.*, have comparable grafted carboxylic acid groups per unit surface area and the ζ -potential of Latex 1 is –41 mV at pH = 2.5, and that of Latex 2 measured at pH = 8 is only slightly higher, *i.e.* –47 mV (see Table 1). Despite a nearly 2× difference in particle size, these latexes have very similar measured μ *vs.* G relationships as shown in Figure 4. A sharp increase in the viscosity, nearly 80× from 6.7 to 520 Pa·s at $G = 1 \text{ s}^{-1}$, is predicted when the pH of Latex 1 is raised from 2.5 to 8.0, as shown by the dashed line in Figure 4. The viscosity of the small sized latex is very sensitive to the thickness of the hairy layer at $c \sim c_m$, especially at low shear rates. Most of these 6 latexes contain ~0.2 M monovalent cations in the aqueous phase, and

this relatively narrow range of the electrolyte concentration in the latex is the main reason that Eq. (4) can be applied to the latexes with widely different „hairy” layer thickness of $1 \text{ nm} < \delta < 5 \text{ nm}$.

The k_o -values for Latex LP-1 by Chu *et al.*, had to be systematically lowered from these predicted by Eq. (4). This latex contains ~0.3 M monovalent counterions as described in the recipe. These include NH_4^+ from the $(\text{NH}_4)_2\text{S}_2\text{O}_8$ initiator, and Na^+ from the anionic surfactant and NaOH used to neutralize methacrylic acid as well as SO_4^{2-} from decomposed initiator. Since the recipe used produces a latex with a solid content of 53%, some of these water had to be removed to prepare dispersions with $c = 0.571$ to 0.621 for the μ -measurement. Therefore, Latex LP-1 could be nearly 1 M Na^+ and NH_4^+ . This is at above the critical coagulation concentration of the dispersion stabilized by the electrostatic forces only. Thus, this latex can be treated as a dispersion of hard spheres with short range electrosteric interactions.

Laun observed that the shear thinning of his ST-ET latex at $c = 0.47$ is drastically reduced by increasing Na^+ concentration in the latex from 0.21 to 1.12 M.^[8] The measured μ dropped from 1.7 Pa·s to below 0.2 Pa·s at $G = 0.1 \text{ s}^{-1}$ but μ -values at $G = 100 \text{ s}^{-1}$ was unchanged at ~40 mPa·s. This nearly 10× reduction in μ at $G = 0.1 \text{ s}^{-1}$ is in exact agreement with a reduction in k_o from 2.98 to 2.50 in Eq. (3), as predicted by Eq. (4) and Eq. (5), respectively, at $Pe = 9.1 \times 10^{-4}$ ($\log Pe = -3.0$). These equations also predict an almost identical k_o -value of 2.3 at $\log Pe = 0$ ($G = 100 \text{ s}^{-1}$) as seen in Figure 2. Eq. (5) for dispersions of hard spheres was established by van de Ven^[5] through analysis of measured μ *vs.* G relationships by Papir and Krieger.^[13] Aqueous dispersions used contained bound charge from the persulfate initiator only at 95% surface saturation of anionic and nonionic surfactants with 6 to 21% anionic surfactant in the presence of 0.1–0.2 M Na_2SO_4 . This particular Na_2SO_4 concentration was chosen at the minimum in the measured μ *vs.*

counterion concentration^[20], and thus the spheres experienced limited interparticle forces. Their work also includes latex particles dispersed into an organic solvent through solvent exchange.^[13] These dispersions in an organic solvent exhibit only weak electrostatic forces in the absence of supporting electrolyte and are expected to behave as hard spheres.

The k_o vs. Pe relationship of Eq. (5) (the dashed line in Figure 2) represents dispersions of hard spheres, and that of Eq. (3) (the solid line in the same figure) is that for soft spheres with ~ 0.2 M monovalent counterions. It is particularly interesting to note that $k_o^\infty \rightarrow 1.70$ for all latexes studied here at $Pe \gg 1$ as predicted by van de Ven.^[5] The k_o vs. Pe relationship for the blend of SP/MP/LP-1 latexes, illustrated by „stars” in Figure 2, maintains a similar trend as that for dispersions of hard spheres (dashed line) but is shifted towards lower Pe -values. The particle trajectories of two colliding spheres in simple shear flow are a strong function of their size ratio^[17], and the time these spheres spend within the separation distance where the colloidal forces become significant decreases sharply as one sphere is smaller than the other. Therefore, a lesser degree of energy dissipation is associated with colloidal particle interactions even at lower shear rates and the electroviscous effect is weaker. Here, a of Latex LP-1 was used to calculate Pe -values for the blend.

Conclusion

The shear thinning behavior of carboxylated latex dispersions has successfully been explained by the modified effective-medium theory proposed by van de Ven.^[5] The model assumes that sheared dispersions always approach close packing at high volume fraction, and that the shear thinning is entirely due to the shear dependence of k_o in Eq. (3). The k_o vs. G relationship has successfully been estab-

lished as a function of Péclet number by Eq. (4) with $k_o^\infty = 1.70$ and $k_o^0 = 3.05$ for carboxylated latexes of 75 nm $< D_w < 250$ nm at $10^{-3} < G < 10^4$ s⁻¹. The k_o^∞ -value is consistent for all latexes examined here at $Pe > 100$, but $k_o^0 \cong 2.50$ for a latex of nearly 1 M Na⁺ concentration. The length of the „hair”, δ , appears to be closely related to the amount and type of functional monomers, and degree of dissociation of carboxylic acid on the latex surface. At high shear the secondary electroviscous effect becomes negligible and the value of k_o approaches the value 1.70 for hard spheres.

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