Cationic Latex: Colloidal Behavior and Interaction with Anionic Pulp Fibers

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ABSTRACT: Styrene–butadiene latexes were prepared in the absence of an emulsifier using a redox initiator $Fe(NO_3)_3/H_2O_2$. Their positive charge was supplied by comonomer *N,N*-diethyl aminoethyl methacrylate. At a given styrene–butadiene ratio (60/40) the particle size depends on the concentration of the comonomer and initiator. The latexes are stabilized by electrostatic repulsion, and remain positively charged and stable up to pH 8. At a higher pH, they acquire a negative charge and restabilize. The positively charged particles deposit readily on negatively charged fibers dispersed in water, thus covering the fiber surface. Upon dewatering and drying, the particles coalesce, and the fibers become covered by a polymeric film, which improves the interfiber bonding and, consequently, the mechanical properties of the fiber assembly. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 1677–1682, 2000

Key words: cationic latex; anionic pulp fibers

INTRODUCTION

The properties of an assembly of fibers, such as a paper, are defined by the type of fiber and the bonding among them. The number of interfiber hydrogen bonds, formed between the surfaces of fibers at the point of their crossing, is rather limited because of microscopic roughness of the fiber surface. Furthermore, they are easily destroyed when exposed to water.

One possibility of increasing the interfiber bonding is to cover fibers with polymeric film and thus form a fiber–polymer–fiber contact. And if the polymer is hydrophobic, the resistance towards water should improve.

The most convenient way of introducing hydrophobic polymer is to use it in the form of latex added to the aqueous suspension of fiber before a sheet is formed. The latex particles must, of course, deposit on the fiber. Upon drying the sheet formed from the latex-covered fibers, the particles will coalesce into a film on the fiber surface.

The main problem is how to achieve a uniform deposition of latex particles to form a continuous film on the fiber surface. The commercially available latexes are negatively charged, and consequently, will not deposit on negatively charged fibers. The use of a cationic polyelectrolyte may encourage a heteroflocculation between the fiber and the latex, but at the same time, cause a homoflocculation of latex particles. This will result in a nonuniform coverage of the fiber by latex aggregates.

Cationic latex offers the possibility of forming monolayer of discrete latex particles covering the fiber. Electrostatic attraction between a positively charged latex and negatively charged fiber governs the deposition, and electrostatic repulsion between latex particles prevents their aggregation.

A number of cationic latexes were prepared by emulsion-free polymerization to test their characteristics and performance—particularly the charge—the stability, and their deposition on fibers suspended in water.

EXPERIMENTAL

Latex Preparation

Distilled water (120 cm^3) in glass bottles (250 cm^3) was purged with nitrogen (15 min). Then redox initiator Fe(NO$_3$)$_3$ 9H$_2$O/30% H$_2$O$_2$ (mass ratio 0.0065/l), styrene ,and *N,N*-diethylamino ethyl methacrylate (DEAEMA) was added, and pH adjusted to 2 with HCl. The bottles were closed, cooled (dry ice + ethanol), and butadiene introduced. The amount of styrene (15 g) and butadiene (10 g) was kept constant, while the amount of DEAEMA and initiator varied. The bottles were rotated in thermostated bath (60°C) for 8 h. After polymerization, the latex was filtered and subjected to vacuum distillation to remove unreacted monomers.

Latex Characterization

Polymer Composition

The content of butadiene in the latex was determined from consumption of bromine, which adds to the double bonds of butadiene.[1] Bromine water (Br$_2$ in saturated KBr) added to the latex was allowed to react for 1 h in the refridgerator. The unreacted bromine was transformed to iodine by adding KJ, and after 15 min, the liberated iodine was titrated with Na$_2$S$_2$O$_3$.

Particle Size

Photon correlation spectrometer (Brookhaven Instrument Co.) with a Bl-0230 Digital correlator and a Spectra Physic 120 He/Ne laser with a wavelength 633 nm was used.

Charge

The electrophoretic mobility of particles was determined using Mark ll microelectrophoresis apparatus (Rank Brothers, Cambridge, UK) equipped with a flat cell.

Colloidal Stability

The rate of destabilization was measured using Photometric Dispersion Analyser PDA 2000

(Rank Brothers, Cambridge, UK). The principle of PDA is based on detecting the change in size that takes place when particles aggregate due to loss of stability.[2,3] The stability is expressed as a stability ratio W = k_i/k_f, where k_i is a given rate, and k_f is the fast rate.

Latex Deposition on Fibers

To the suspension of 1 g of fiber in 500 mL water, kept under slow (80 rpm) paddle stirring, an appropriate amount of latex was added. A sample of supernatant was withdrawn by syringe equipped with a filter tip to exclude fibers. Light transmittance of the sample was converted to concentration using the established linear relationship between log transmittance and concentration.

The difference between the amounts of latex added and found in the supernatant is the amount deposited on the fibers. The kinetic of deposition was determined by taking samples in timed intervals starting 15 s after the latex addition.

RESULTS AND DISCUSSION

Particle Size—Effect of Comonomer and Initiator Concentration

According to the emulsion polymerization theory of Fitch,[4] the particle formation rate can be expressed as

$$\frac{dN}{dt} = bR_i - R_c - R_f$$

in which N is the number of particles per unit volume at time t, b is the fraction of oligoradicals reaching critical chain length for nucleation, R_i is the generation rate of free radicals, R_c the rate of free radicals captured by the particles, and R_f the rate of change in the number of particles due to coagulation. Based on this theory, high R_i or low R_c and R_f values should result in a large number of small particles with a narrow distribution in particle size.
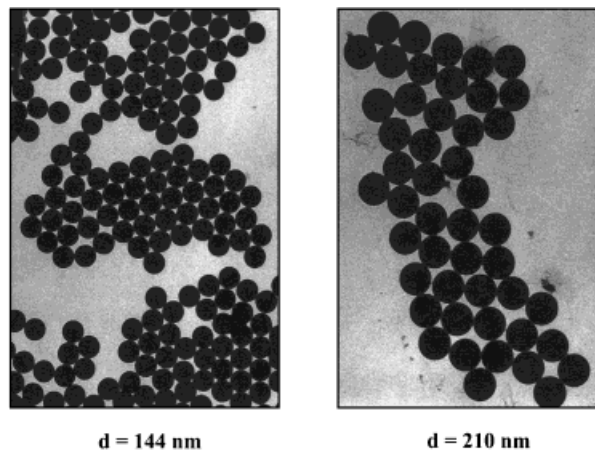
Factors that may affect R_i, R_c, or R_f, and hence, the particle size are: (a) the concentration of initiator; (b) the concentration of the monomer and the comonomer; (c) the concentration and the structure of the emulsifier; (d) the solvent; and (e) the mode of addition.

The effect of the cationic comonomer concentration at a constant level of the initiator is shown in Figure 1(a). The observed decrease in size with increasing content of comonomer is likely related to its role as an in situ-formed emulsifier. In the emulsifier-free system, the water-soluble ionic comonomer interacts with the main water-insoluble monomer (styrene, butadiene), thereby forming a product that has both hydrophobic and hydrophilic parts. Thus, it has a tendency to locate at surface of the forming latex particle, and besides providing the particle with a positive charge, it acts also as an emulsifier (surfactant). With increasing concentration of the ionic comonomer more (and, therefore, smaller), particles can be formed.

The effect of the initiator concentration at a constant level of the cationic comonomer is shown in Figure 1(b). The size of the latex particles increases with increasing the level of the initiator, which appears to be contrary to expectation. Two possible explanations may account for this. The first—in the initial stage of polymerization the number of primary particles increases with increasing amounts of initiator, but if their charge is not sufficient to stabilize them, they coagulate and form bigger particles. The second—with increasing amounts of the redox initiator the ionic strength increases, and consequently, the electrostatic repulsion among particles decreases, resulting in coagulation. The latexes of different size were all reasonably monodisperse as shown in Figure 2.
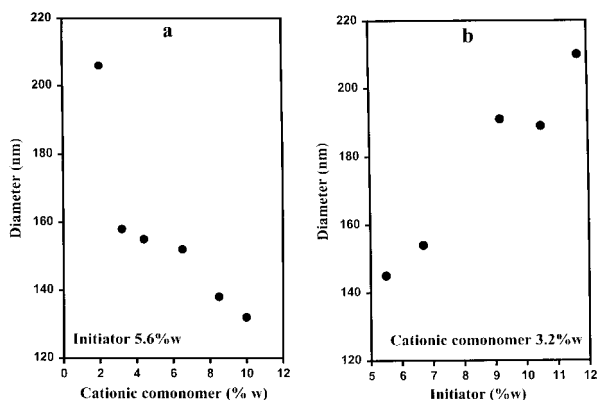
d = 144 nm   **d = 210 nm**

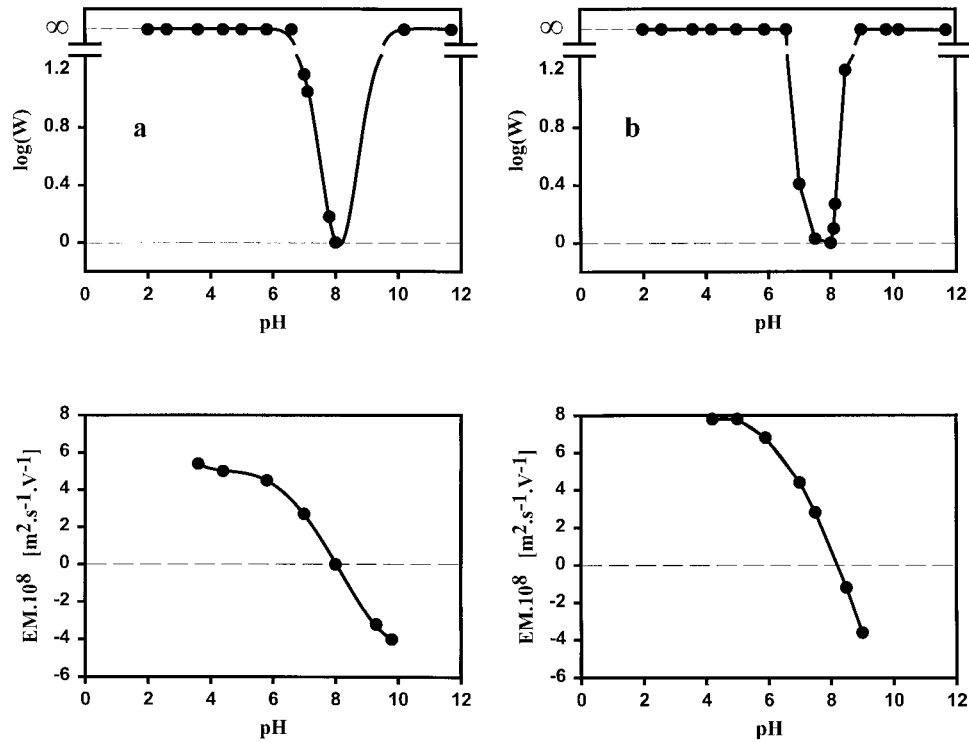**Figure 2**   Micrographs of latex particles 144 and 210 nm in diameter.

Stability

The colloidal stability of latex prepared by emulsifier-free polymerization results from the electrostatic repulsion of charged particles. The positive charge is provided by the comonomer tertiary amino groups, the dissociation of which is pH dependent. The dissociation, and consequently, the charge, increase with decreasing pH. The classical theory of stability of hydrophobic colloids predicts that as long as there is a sufficient charge, the particles remain dispersed. When the charge, and consequently, the mutual repulsion, drops below a certain value (around 0.5 kT), the attractive van der Waals forces cause aggregation of the particles, i.e., the system destabilizes.

All the experimental cationic latexes behave as expected. As an example, in Figure 3 the electrophoretic mobility and stability of latex prepared with 3.2 wt % DEAEMA (a) for latex prepared with 8.5 wt % DEAEMA (b) is shown. Below pH 6, the latexes are positively charged and remain stable, as shown by the stability ratio $W = \infty$. Because the W is expressed as the ratio of the fast destabilization to the given rate, log $W = 0$ means an unstable system. The higher values of W thus indicate that the system destabilizes, but at a slower rate.

In an agreement with this theory, the fast destabilization takes place around pH 8 when particles become uncharged. Above pH 8, the particles acquire a negative charge and restabilize due to the electrostatic repulsion.
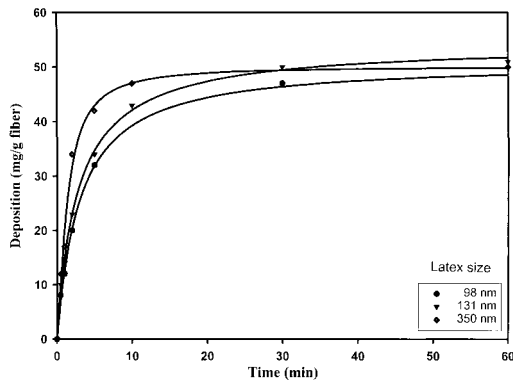
Deposition on Fibers

In a system composed of negatively charged fibers suspended in water, the positively charged latex

Figure 1   (a) Size of latex particles as a function of cationic comonomer (DEAEMA) concentration at constant level of initiator. (b) Size of latex particles as a function of initiator concentration at constant level of cationic comonomer.

Figure 3   Stability ratio (log $W = \infty$; stable; log $W = 0$ fast coagulation) and electrophoretic mobility as a function of pH. Latex prepared with 3.2% DEAEMA (a) and 8.5% DEAEMA (b). Initiator concentration 5.6% w.

particles should deposit on the fibers due to mutual electrostatic attraction. In Figure 4 a deposition as a function of time of three latexes having different sizes and added in the amount of 50 mg per gram fiber is shown.

From Figure 4 it is obvious that all the added latex ends up on the fibers, and that the rate of deposition increases with an increased size of the particles, which is in agreement with prediction.[5]

The stable latex is expected to deposit as individual particles, thus forming on the available surface of the fibers a monolayer. If this assumption is correct, than with an increasing addition of the latex a limit in the amount of the deposited latex will be reached. This is shown in Figure 5,

Figure 4   Deposition on fibers as a function of time for latexes of different size added in the amount of 50 mg per gram fibers.
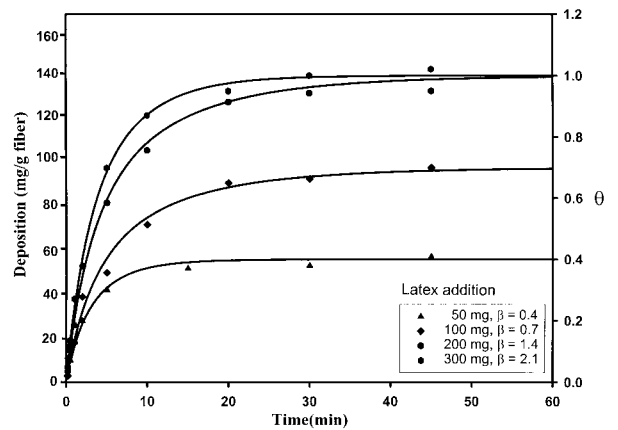
Figure 5   Deposition of latex (255 nm) on fibers as a function of time. Latex addition 50–300 mg per gram fibers. β = amount of latex added/maximum deposition (140 mg/g fiber).

where a maximum of 140-mg latex deposits on 1 g of fiber. This amount is close to the calculated value, assuming closely packed spheres covering 1 m^2, which is often quoted as the external surface area of 1 g of fibers. For latex particles of a density of 1 and a diameter of 255 nm, the calculated amount is 130 mg/g if packing is regular, and 150 mg/g if it is hexagonal.

The rate of deposition can be treated by an analogy with the Langmuir analysis of gas molecule adsorption.[6,7] However, because often there are not enough particles in the system to cover the available surface fully, a modified version describes the rate of deposition:[8]

$$\theta = \frac{1 - \exp[(1 - \beta)\alpha_o k_{12} N_f t]}{1 - \beta^{-1}\exp[(1 - \beta)\alpha_o k_{12} N_f t]}$$

where θ is the fractional surface coverage of fibers by latex particles, α_o is the collision efficiency factor, k_{12} is the rate constant of collisions between fiber and latex, N_f is the number of fibers, and t is time. The parameter β is of particular importance, because it reflects the ratio between the number of particles present and the maximum number of latex particles that may deposit on the available surface. Thus, the equation describes the rate of particle deposition under a condition where the number of particles present exceeds the number that can deposit, $\beta > 1$, as well as where there is a shortage, $\beta < 1$.

Comparison of Experimental and Theoretical Rate Constants

From the best fit through the experimental points, in Figure 5 the value $\alpha_o k_{12} N_f = 2.5 \times 10^{-3}$s^{-1} was found. The number of fibers N_f in a unit volume (m^3) can be estimated from their average length of 2 mm, and the mass per unit length 0.1 mg m^{-1}. At the fiber concentration, 1 g in 500 cm^3 $N_f \approx 1.10^{10}$ m^{-3}, which gives $\alpha_o k_{12} \approx 2.5 \times 10^{-13}$m^{3}s^{-1}.

The theoretical rate constant k_{12}, according to Smoluchowski,[9] can be calculated for either perikinetic (diffusion controlled) or orthokinetic (shear-induced) collision between unequal spheres in uniform shear.

$$\text{Perikinetic} \qquad k_{12} = \frac{2kT(a_1 + a_2)^2}{3\eta a_1 a_2}$$

$$\text{Orthokinetic} \qquad k_{12} = 4(a_1 + a_2)^3 G/3$$

where a_1 and a_2 are the radii of the spheres, G is the shear rate, and $2kT/3\eta = 3.1 \times 10^{-18}$m^{3}s^{-1}, η being the intrinsic viscosity. The size of fibers represented by a cylinder of length $L = 2$ mm and of radius $R = 15$ μm can be expressed in terms of an effective radius by replacing the volume of the cylinder with the effective sphere.[5] Hence $\alpha_{\text{eff}} = (3/4\ R^2 L)^{1/3} \approx 70$ μm.

Due to the size of colliding particles (fibers and latex) the process can be considered orthokinetic and, therefore, calculated $k_{12} = 4.5 \times 10^{-13}m^3 \cdot G$. The shear rate G (s^{-1}) in our system is not uniform, and is difficult to evaluate. From the mixing rate (80 rpm) and geometry of the system it is estimated to be around 10 s^{-1} and, therefore, the $k_{12} \approx 4.5 \times 10^{-12}$ m^{3}s^{-1}. Hence, by comparing with the experimentally obtained value α_o K$_{12}$ $\approx 2.5 \times 10^{-13}$m^{3}s^{-1} the efficiency factor α_o, which depends on the ratio of attractive and shear forces, is around 0.05. This is a reasonable value for the orthokinetic capture efficiency between unequal sized particles for $G = 10$ s^{-1}.[5] Thus, the observed deposition rate is consistent with Smoluchowski's kinetics.

Interfiber Bonding

Tensile strength of paper is a function of total energy of interfiber bonding, which means the number of hydrogen bonds formed within the area of fiber crossing. Due to the surface roughness, only small fractions of fiber surfaces are close enough (0.3 nm) for hydrogen bonding to occur. When latex particles deposited on the fiber coalesce and form a film upon drying, the result is a smoother surface, and thus increased probability of additional interfiber bonding. The SEM of the fiber surface, its coverage by individual latex particles, and the surface covered by polymeric film is shown in Figure 6.

In Figure 7 an example of the improvement in mechanical properties of handsheets formed from fibers treated with different amounts of cationic latex diameter (155 nm) is shown. Both the tensile strength and the elongation at break increase simultaneously, and consequently, the tensile energy absorption also increases.

CONCLUSION

Styrene–butadiene latexes prepared by emulsion-free polymerization in the presence of comonomer N,N-diethylaminoethyl methacrylate
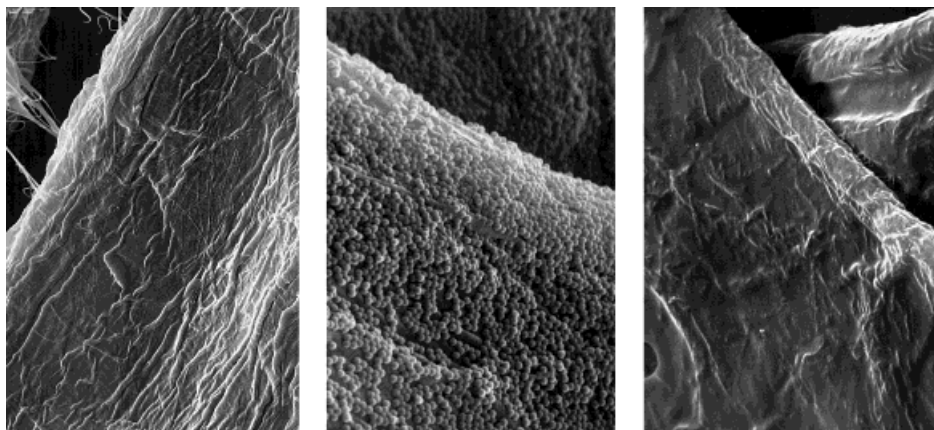
Figure 6   Scanning electron micrographs of the original fiber surface (left), coverage of fiber by deposited latex (middle) and polymeric film formed when latex particles coalesce (right).
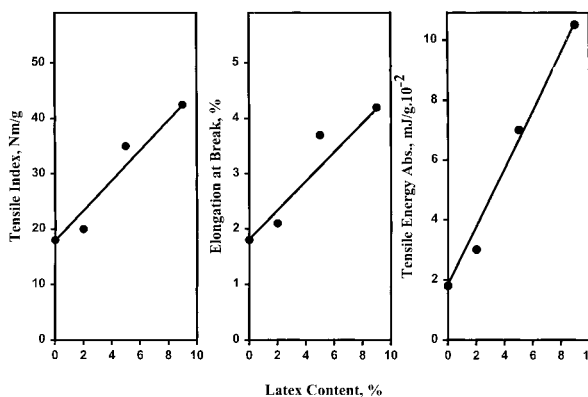
are positively charged and stabilized by electrostatic repulsion. The cationic latexes deposit readily on anionic fibers suspended in water, and form a monolayer on fiber surface. Upon dewatering and drying, the fibers are covered with a poly-meric film that improves the bonding between fibers.

Figure 7   Improvement in mechanical properties as a function of latex content of hand sheets formed from fibers treated with cationic latex.

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