Deposition of Clean and Contaminated Latex Particles on Pulp Fibers

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ABSTRACT: Electrostatic interaction between latex particles and oppositely charged surfaces can be affected by the presence of ionic compounds, which are not an integral part of latex particles. They could be formed during polymerization or could be present as emulsifiers. This "free charge" adsorbs on fiber and interferes with latex particles deposition. Consequently, with increasing latex addition, the extent of deposition may decrease. Attempts to explain such unexpected behavior often lead to questionable conclusions. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 98: 1879–1883, 2005

Key words: fibers; latices; deposition; adsorption; contaminants

INTRODUCTION

Modification of surface characteristics of pulp fibers is often done by adsorbing cationic water soluble polyelectrolytes on anionic fibers suspended in water. However, when an introduction of hydrophobic polymer is desired, the most convenient way appears to be to use them in the form of latex. Provided that the latex and the fibers are oppositely charged, it is expected that due to electrostatic attraction the latex particles will deposit on fibers. Upon forming a sheet from such latex-covered fibers, dewatering and drying, the latex particle will coalesce into a film on the fiber surface. This means that the natural interfiber bonds are replaced by fiber–polymer–fiber bonds and thus, the mechanical properties of the sheet are affected. The sheets also become water repellent because the fibers are covered by a hydrophobic polymer. To be most effective, the polymer should cover fibers uniformly, which can be achieved by forming a monolayer of discrete particles on the fiber surface.[1,2] This will happen when the repulsion between particles, which are driven to the fibers by electrostatic attraction, is strong enough to prevent their homocoagulation.

The logical assumption that latex particles would deposit on oppositely charged fibers is often not fulfilled, particularly, when dealing with commercial latices. The latex particles might deposit in an amount that is far less than that required for a full coverage of fiber surface or might not deposit at all. Such experience could lead to a premature dismissal of the whole idea and could cast a doubt concerning the applicability of the basic rules of colloidal interaction. The intention here is to explain such behavior and to document that the deposition of latex particles on oppositely charged fibers takes place as expected, providing that the conditions are right. The process of deposition is affected when the system is contaminated by interfering substances.[3,4] These are ionic compounds present as a "free charge" *i.e.*, not an integral part of latex particles.

EXPERIMENTAL

Materials

Anionic fibers

Softwood bleached kraft pulp washed several times to remove fines. The charge determined as electrophoretic mobility (EM) = -1.7×10^{-8} m^2 s^{-1} V^{-1}.

Cationic fibers

Fibers suspended in water treated with 50 mg polyethylenimine (PEI) per gram fiber. After 30 min of continuous mixing, the fibers were separated and washed several times to remove unadsorbed polymers. The charge determined as EM = $+2.5 \times 10^{-8}$ m^2 s^{-1} V^{-1}.

Cationic latex

Polystyrene experimental sample, 0.5 μm in diameter, supplied by Hercules. EM = $+1.5 \times 10^{-8}$ m^2 s^{-1} V^{-1}.
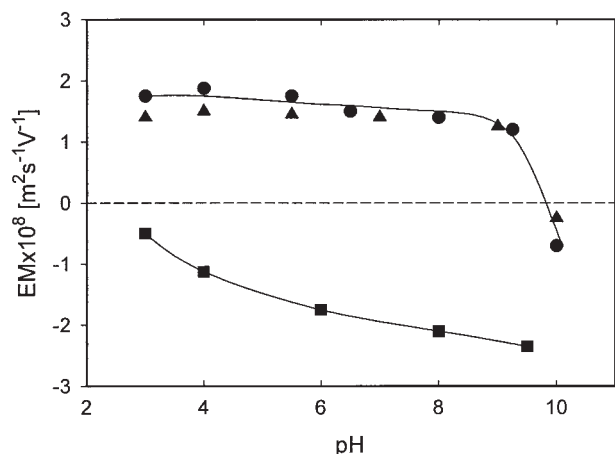
Figure 1 Electrophoretic mobility as a function of pH for cationic latex original (▲), cleaned (●), and pulp fibers (■).

Anionic latex

(1) Polystyrene standard, 0.48 μm, from DOW Chem. EM = -2.3×10^{-8} m^2 s^{-1} V^{-1}. (2) Polystyrene 0.75 μm from GenCorp. EM = -3.0×10^{-8} m^2 s^{-1} V^{-1}.

Methods

Latex deposition on fibers

A suspension of 1 g of fibers in 500 mL water was kept under slow (80 rpm) paddle stirring, and an appropriate amount of latex was added. A sample of supernatant was withdrawn in timed intervals by a 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 amount of latex added and that found in the supernatant is taken as the amount deposited on fibers. The amount of deposited latex reported is the maximum observed.

Latex cleaning

Removal of "free charge" was done using fibers as a scavenger. Latex was added to fibers suspended in water and after 15 min of mixing, the fibers were separated by filtration. The "free charge" adsorbed on fibers is thus eliminated and the latex remaining in the supernatant is used for deposition studies. When the concentration of the "free charge" is too high and consequently still present in the latex after cleaning, the procedure is repeated. The efficiency of cleaning is evaluated from change in stability measured as a function of oppositely charged polyelectrolyte addition. (See Fig. 2 for an example.)

Colloidal stability

The stability is expressed as a stability ratio log W = K_f/K_i where K_i is the given rate of destabilization, and K_f is the fast rate. This means that for log $W = 0$ the system is unstable and for log $W = \infty$ it is stable (within a given period of time). At log $W > 0$ the system destabilizes, but at a slower rate. The rate of destabilization was measured using a Photometric Dispersion Analyzer, PDA 2000 (Rank Brothers, Cambridge, UK). The principle of PDA is based on detecting the change in size that takes place when particles aggregate because of loss of stability.[5]

Charge

The EM of particles was determined using a Mark II microelectrophoretic apparatus (Rank Brothers) equipped with a flat cell.

RESULTS AND DISCUSSION

Cationic latex—anionic fibers

Characterization of cleaned and contaminated latex

The EM measured as a function of pH does not reveal significant difference between the latices, as seen in
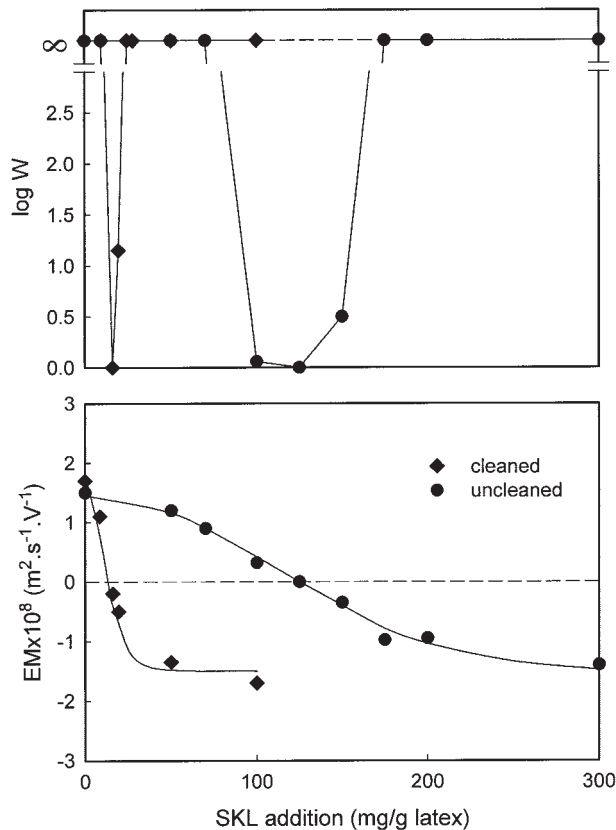

Figure 2 Stability and electrophoretic mobility of cationic latex as a function of anionic sulfonated kraft lignin (SKL) addition. Log $W = \infty$ means colloidaly stable up to 60 min. Log $W = 0$ means fast coagulation.
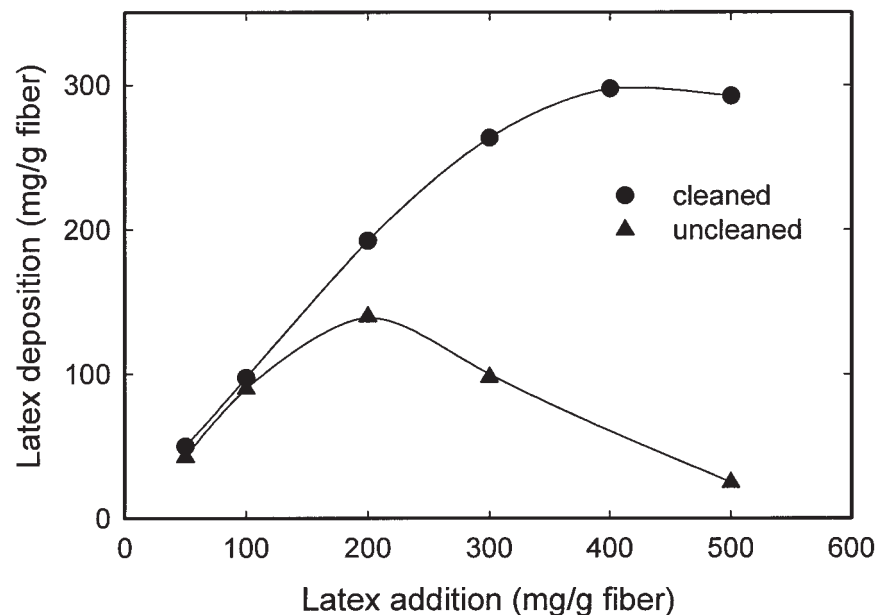
Figure 3   Maximum deposition of original and cleaned cationic latex on anionic fibers as a function of latex addition.

Figure 1. Included are also data for the pulp fibers. From the graph, one may conclude that up to pH 9 the positively charged particles of both cationic latices will deposit on anionic fibers suspended in water. However, there is a difference between the latices, which becomes apparent when comparing their stability and EM measured as a function of anionic polyelectrolyte SKL (sulfonated kraft lignin) addition shown in Figure 2. As seen in the upper part, the cleaned latex requires addition of about 15 mg SKL per gram of latex to destabilize and consequently to aggregate. Since at the same SKL addition the latex charge is neutralized, as
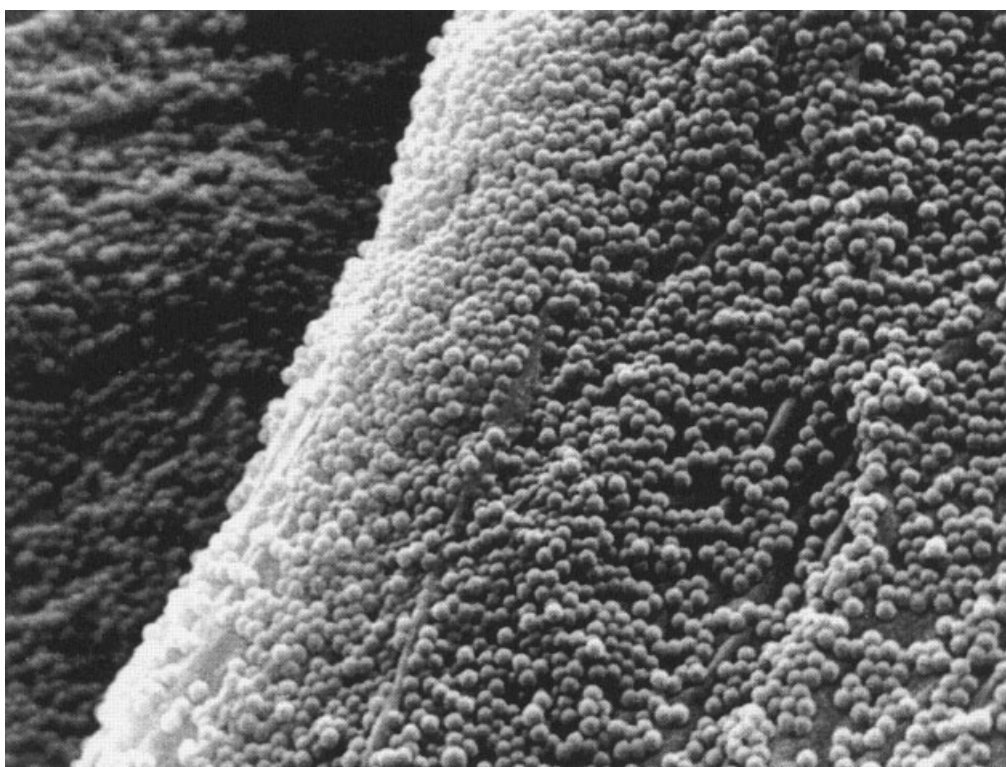

Figure 4   SEM observation of latex particles deposition on fiber surface.
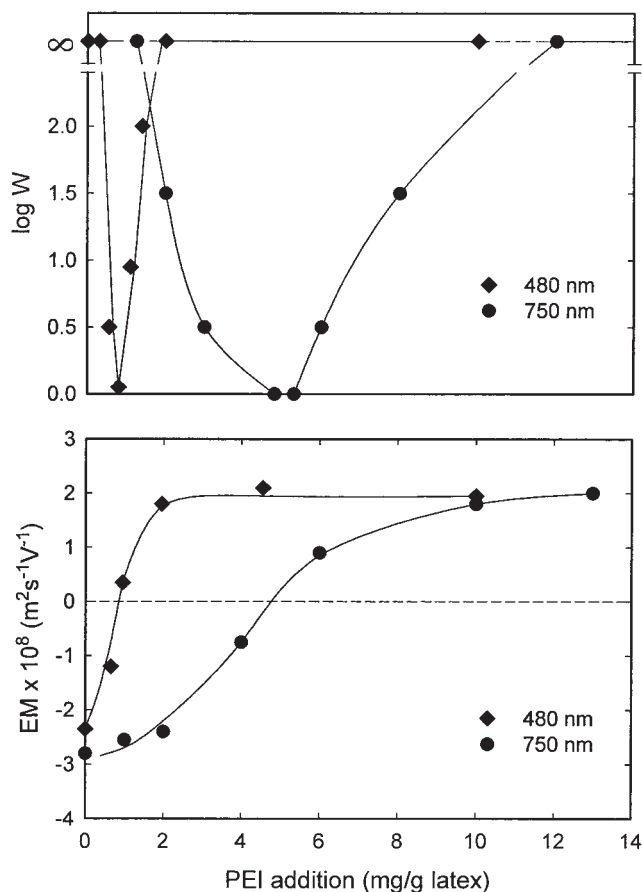
Figure 5 Stability and electrophoretic mobility of two anionic latices (0.48 and 0.75 μm) as a function of cationic polyethylenimine (PEI) addition. Log $W = \infty$ means colloidaly stable up to 60 min. Log $W = 0$ means fast coagulation.

shown in the lower part, the behavior indicates that the system is electrostatically stabilized. The original latex requires considerably more SKL, about 100–120 mg, to destabilize and neutralize 1 g of latex. The difference represents the amount of "free charge" in the latex, *i.e.*, the charge that is not an integral part of the latex particles and was removed by cleaning. This may be a cationic compound formed during polymerization or present as emulsifier. By forming a complex with the anionic SKL, the "free charge" is eliminated at the expense of increased consumption of SKL.

Deposition of cleaned and contaminated latex

Figure 3 shows maximum deposition as a function of latex addition. The original latex deposits almost completely up to 100 mg addition per gram fiber. At 300 mg addition it deposits less than at 200 mg addition. Further decease is observed at 500 mg addition. This behavior appears to be because of the presence of cationic "free charge." By adsorbing on fibers, it makes them less attractive to latex and depending on its

concentration, it may prevent deposition completely. The result is the often confusing observation that the more latex is added the less it deposits on oppositely charged fibers or other substrates.

The expected behavior is demonstrated by using the cleaned latex. As shown in Figure 3, deposition increases with increased addition reaching a maximum at about 300 mg latex per gram fiber. This is close to the amount calculated for a full coverage of fiber surface (about 1 m^2 g^{-1}) by a monolayer of densely packed spherical particles 0.5 μm in diameter. The actual situation observed by scanning electron microscope is shown in Figure 4.

Anionic latex—cationic fibers

Characterization of latex

Two anionic latices were used. Their stability and EM as a function of cationic PEI is shown in Figure 5. The smaller latex requires about 1 mg PEI per gram to destabilize and become uncharged. The larger one requires about 5 mg PEI.

Deposition on fibers

Figure 6 shows deposition as a function of addition of the smaller anionic latex on cationic fibers. All the latex deposits up to 300 mg addition per gram fiber. Apparently, this amount is sufficient to form a monolayer of discrete particles on the available fiber surface because larger addition does result in more deposition. The overall behavior indicates the absence of anionic "free charge," which would interfere with the latex deposition.

The larger latex behaves differently, as shown in Figure 7. A quantitative deposition is observed up to 200 mg addition for both the clean and the unclean
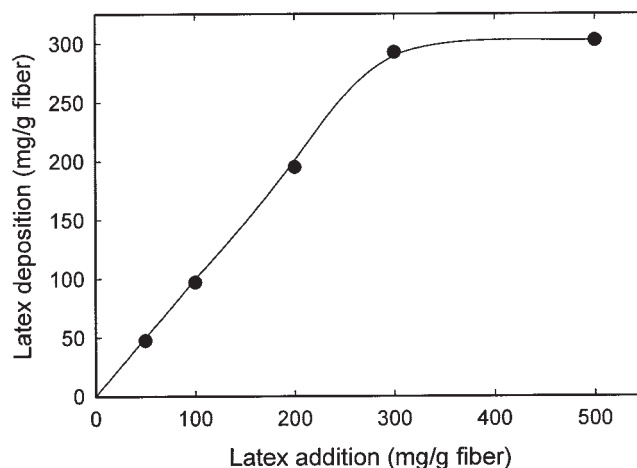

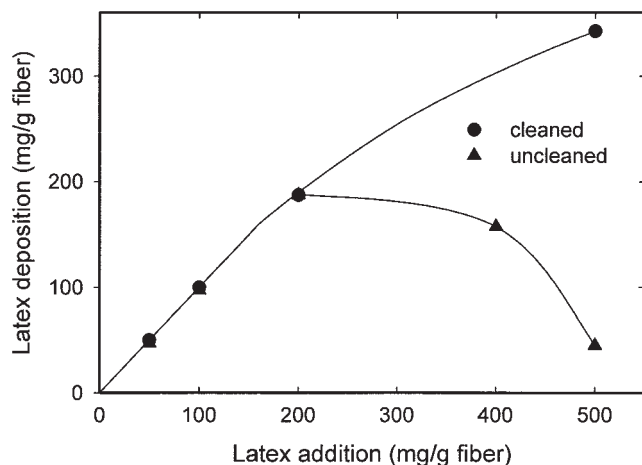**Figure 6** Maximum deposition of anionic latex, 0.48 μm, on cationic fibers as a function of latex addition.

Figure 7 Maximum deposition of original and cleaned anionic latex, 0.75 μm, on cationic fibers, as a function of latex addition.

latex. Afterwards, deposition of the original latex decreases. That this is due to "free charge" is demonstrated by cleaning. When the anionic "free charge" is eliminated by using cationic fibers as scavengers, the deposition at 500 mg latex addition increases up to 350 mg per gram fibers.

CONCLUSIONS

When dealing with a realistic system, the presence of "free charge" and its effect on latex-fiber (or other substrate) electrostatic interaction must be considered. Excess of "free charge" delivered by latex is detrimental to latex deposition on fibers dispersed in water because it adsorbs on fibers and makes them less attractive. This leads to erratic results and consequently to either wrong conclusions or doubts about the applicability of the basic rules of colloidal interactions.

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