

Latex-Fiber Interaction and Paper Reinforcement

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Synopsis

A model system for studying the reinforcement of paper is provided by the use of cationic latexes. The control of pH during addition of the latex to the pulp determines the uniformity of the latex deposition on the fibers. It is demonstrated, using scanning electron microscopy and mechanical testing of the sheet, that the dry and wet strength properties are improved by the more uniform distribution of a film-forming latex. Conversely, a nonfilming latex impedes bonding to the extent that the fiber surface is covered.

INTRODUCTION

The introduction of polymers into paper is frequently achieved in practice by the wet-end addition of latexes. The deformation and failure properties of the sheets are modified by such additives, and a wide variety of products are obtained depending on the amount and nature of the latex that is incorporated.

The retention and distribution of latexes added to the stock before sheet formation are determined by colloidal phenomena. Conventionally anionic (negative) latexes are deposited on negatively charged fibers by procedures, sometimes quite complicated, involving coupling agents, electrolyte addition, and resins. The precipitation is usually induced by an additive that reduces or reverses the charge on the fiber so that the latex is deposited. A competing reaction is the coagulation of the latex particles themselves, and a concurrent result can be the increased flocculation of the fibers. One of the most commonly used deposition aids is alum, which can coagulate the anionic latex and simultaneously can alter the charge on the latex particles or fiber surfaces.

The properties of the paper depend upon the sequence and manner of the introduction of the latex and other additives to the stock as well as on the amount of latex. Studies of the conditions of the addition¹⁻⁶ suggest that the latex particle distribution plays an essential role. There has been some controversy,^{1,4} if not much evidence, on the question of whether the latex should be uniformly distributed or whether it should be deposited as aggregates to produce optimum results.

This paper reports some model experiments that were designed to demonstrate the role of latex deposition in interfiber bonding and thus on the properties of the sheet. The latex used was cationic in nature in order to facilitate

its retention on negatively charged fibers. The stability of latex was controlled by pH in an attempt to regulate the latex deposition from an even coverage of fibers to a sparse coverage by larger latex aggregates.

EXPERIMENTAL

Materials

Pulp Fibers. Kraft unbleached unbeaten; carboxyl content, 8.8 mmole/100 g; α -cellulose, 81%. Disintegrated fibers were washed three times with distilled water in order to remove fines which were observed to attract the latex preferentially, thus interfering with an even coverage of the fibers by latex particles.

Latex. An experimental cationic film-forming styrene-butadiene latex was prepared in the absence of emulsifier⁷ using H_2O_2 and $Fe(NO_3)_3$ as initiator. A reaction bottle, kept at 5°C, was charged consecutively with 120 g deionized water, 7.1 mg ferric nitrate, 1 g 2-(diethylamino)ethyl methacrylate (DEAEMA), hydrochloric acid to pH 2, 18 g styrene, and 0.6 g hydrogen peroxide. The bottle was sealed with a special cap and cooled in acetone-dry ice mixture. By means of a needle penetrating the cap, 16.84 g butadiene was added. Then the bottle was secured in a metal cage and tumbled in a constant temperature bath at 60°C for 8 hr, the latex was then subjected twice to flash evaporation to remove the unreacted monomers. Since neither emulsifier nor salt was used during polymerization, no further purification was used. The monomer conversion was 54.5%, and the solid content of the final product was 23.3%. The latex was reasonably monodisperse with particle size approximately 0.15 μm and contained 35% butadiene determined by a titration method based on the addition reaction of bromine ions to the double bonds in the styrene-butadiene molecule.⁸

Latex Addition and Sheet Formation

An appropriate amount of latex diluted in 100 ml water was added to a fiber suspension (1 g in 400 ml) under slow (90 rpm) paddle stirring, and pH was adjusted by means of HCl and NaOH. After 30 min of stirring, the suspension was transferred into the standard sheet-forming apparatus. Throughout the whole procedure, only distilled water was used. The sheets were normally dried at room temperature. It was found that strength development continued with heating, and duplicate handsheets were further heated to 105°C for 5 hr.

Parallel samples for observing the effect of nonfilm-forming latex incorporated in the sheet were employed. The procedure was the same as described above; but before sheet formation, the sample was dewatered, the wet web was brominated in order to harden the latex and prevent its further coalescence,⁹ and again redispersed. Electron-microscopic observation showed that the water removal by filtration did not cause coalescence of the latex deposited on fibers. The bromination served simultaneously for determination of the latex content of the sheet described below. The redispersion of brominated fibers was found to alter the amount of latex attached to the fibers only marginally.

Latex Retention

The amount of retained latex was determined separately for the fibers and the sheet because the total amount of latex in the formed sheet may differ from the latex deposited on the fibers in the latex-fiber suspensions. When the suspension is diluted in the sheet machine, some of the weakly attached latex may redisperse or, alternatively, the unattached latex remaining in the suspension may be retained during the sheet formation by a filtration effect.

The retention of latex in the fiber suspension was determined from the change in latex concentration during the mixing period by means of turbidity measurement. The calibration for turbidity was established for the whole range of pH and was found essentially the same up to pH 6 and above pH 8.

The total amount of latex in the formed sheet was determined by means of bromine consumption.⁸ The wet web formed in a sheet machine was dispersed in 250 ml water in a glass-stoppered flask, 10 ml 0.2*N* Br₂/KBr was added, and kept in darkness at 4°C for 1 hr. Then, 10 ml 20% KI solution was added, and after 15 min the suspension was titrated with 0.2*N* Na₂S₂O₃ solution to the starch endpoint. The bromine consumption of latex alone was obtained by subtracting the amount of bromine consumed by the fibers as determined on blank samples without latex. The amount of latex was then calculated from the known specific bromine consumption of the particular latex.

Latex Deposition

Scanning electron microscopy (SEM) was employed for observing the latex distribution on individual fibers and in sheet. Wet samples of fibers were taken from the suspension in the sheet machine and brominated in order to prevent a coalescence of latex particles upon drying. The samples were allowed to dry on a microscope mount and metalized with gold-palladium alloy.

To determine the latex distribution in the sheet, the sheet was formed from brominated fibers. The observation was made on fibers located on the surface as well as within the sheet by removing the outer layer of fibers.

Tensile Test

Strips 15 mm wide were conditioned at 22°C and 60% R.H. and tested for both dry and wet tensile strength. The strips for wet tensile were soaked for at least 15 hr in distilled water containing a surface-active agent (Triton X-100) in order to facilitate complete wetting.

Electrophoretic Mobility

A Zeiss cytopherometer adapted for a dark-field observation was employed for determining the effect of pH on the electrophoretic mobility of latex particles. The mobility was measured in the actual environment in the absence of salt.

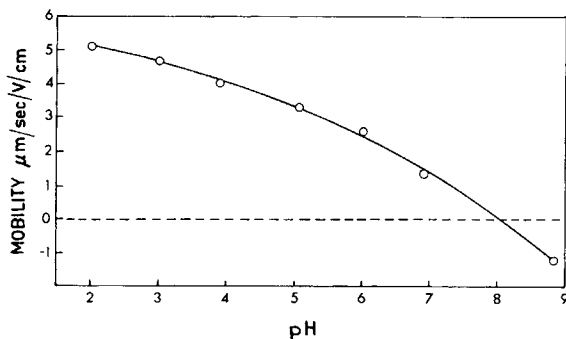


Fig. 1. Electrophoretic mobility of styrene-butadiene latex as a function of pH.

RESULTS AND DISCUSSION

The experiments were designed to vary systematically the deposition of the latex on the fibers and to determine the effect of this variation on the dry and wet strengths of the handsheets formed from the treated fibers.

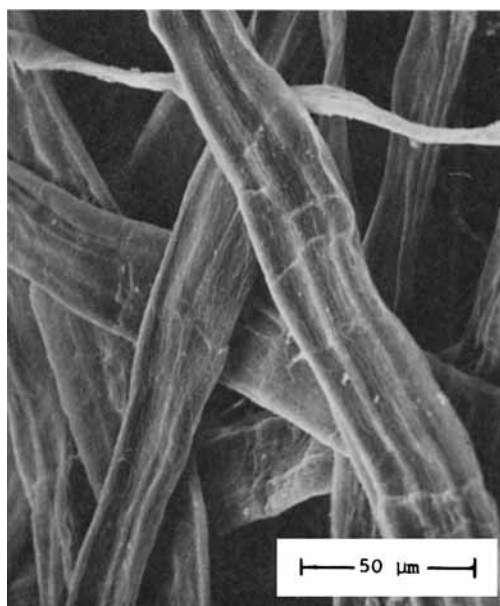
Controlled Latex Deposition

The method chosen for varying the distribution of latex was pH control. As the pH is increased from a low value the mobility of the latex particle falls and the stability of the latex decreases until, at pH 7, the latex coagulates easily. Above pH 8, the charge of latex is reversed (Fig. 1). The electrical surface properties of fibers, due to their negative charge, generally display an opposite trend. The negative value of mobility decreases toward lower pH and reaches zero around pH 2.5.¹⁰

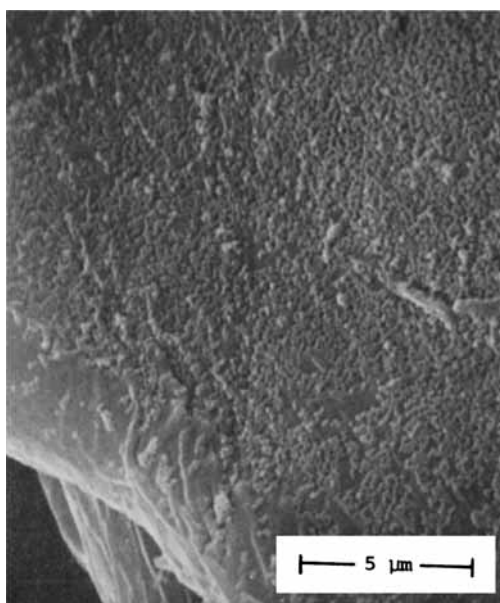
It was expected that, owing to the higher stability at low pH, the latex would deposit as individual particles, ideally covering the fiber surface as a monolayer. The amount of latex required for a full coverage of fibers in form of monolayer can be estimated only roughly. If the external surface of fibers is between 0.5 and 1 m²/g,¹¹ 0.05–0.1 g of closely packed latex particles 0.15 μm in diameter will cover 1 g of fibers. At higher pH, the tendency for latex coagulation would cause the latex to deposit in the form of aggregates. In the systematic investigation, two levels of latex (5% and 10%) were added to pulp fibers at controlled pH's between 2 and 9.

The effects of pH control on latex distribution can be seen directly from scanning electron micrographs (Figs. 2–5). At the lowest pH, the latex is distributed more or less as a monolayer of particles. At higher pH, there is a progressively increasing incidence of latex aggregates until, at the highest pH, the zeta potential is reversed in sign so that little latex is observed on the fibers.

It was of obvious interest to find whether the latex distribution observed on dispersed fibers was maintained after sheet formation and that no migration occurred during drying. The latex distribution was observed on fibers located on the surface of a formed sheet as well as on fibers located inside the sheet. There was no significant difference between the outer and inner fibers and the deposition at various pH was similar to that of dispersed fibers.



(a)

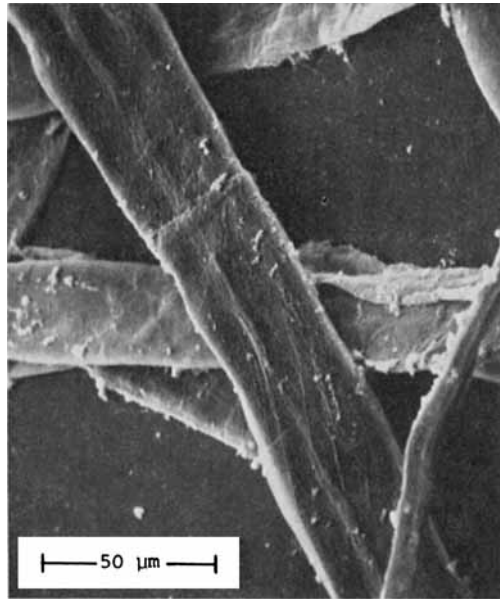


(b)

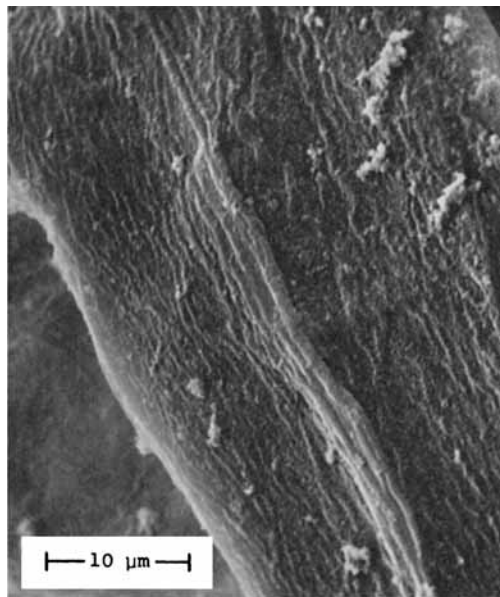
Fig. 2. Latex deposition on unbeaten kraft fibers at pH 2 observed by SEM at two magnifications. The fiber surface is predominantly covered by individual latex particles.

Latex Retention

The latex retention is recorded for two levels of addition (5% and 10%) in Figure 6. Data for both the latex retained by suspended fibers and the amount of latex in formed sheets are shown. At the 10% level, complete retention is only obtained when the latex deposits as aggregates. At lower



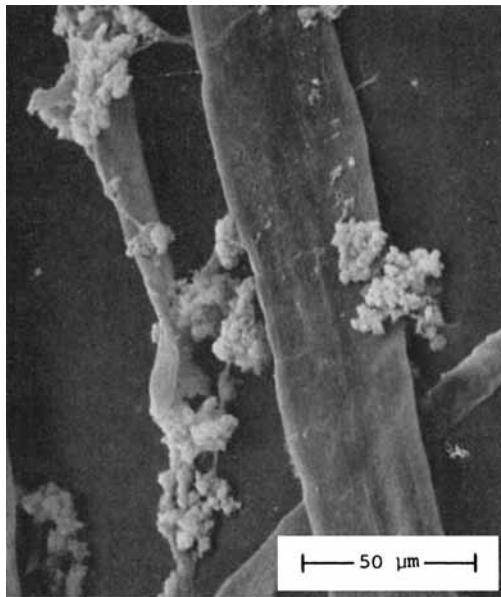
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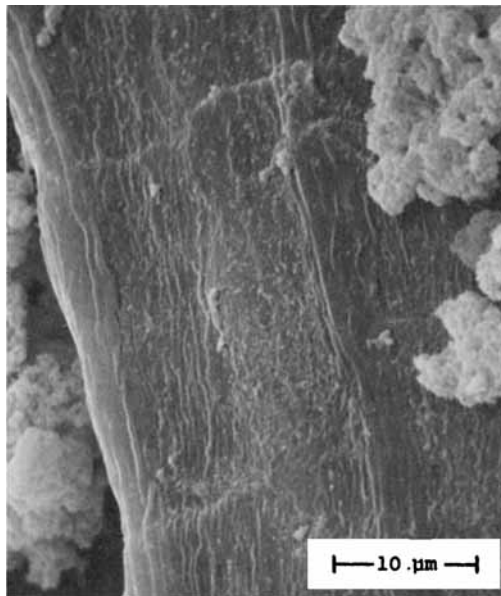
(b)

Fig. 3. Latex deposition at pH 4. The fiber surface is still covered by a layer of individual particles but a number of aggregates is already present.

pH's, the amount of deposited latex is likely limited by the extent of fiber surface available and possibly by the decreased negative charge of fibers which diminishes the fiber-latex attraction. At pH 9, there is no retention except by a filtration effect during sheet formation.



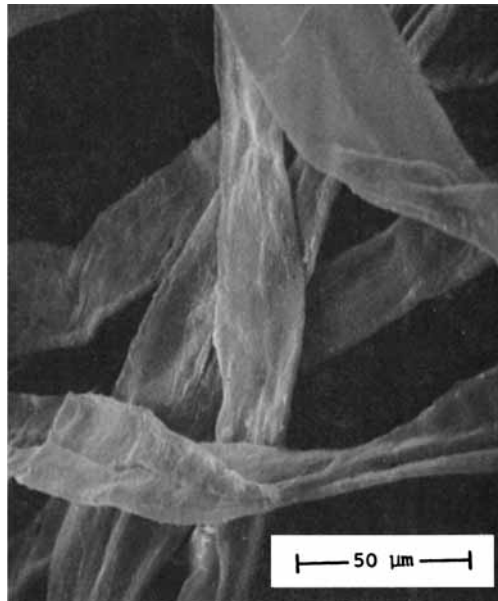
(a)



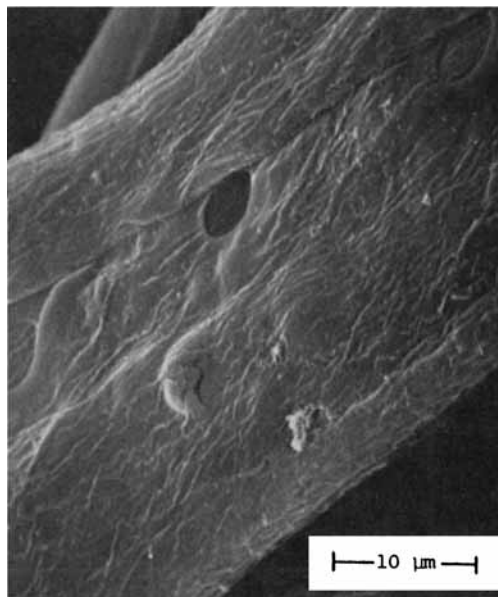
(b)

Fig. 4. Latex deposition at pH 7. The latex predominantly deposits in the form of large aggregates.

At the 5% level, the retention is substantially complete although at low pH's, some fall-off is noted, possibly due to the decreased negative charge on the fibers.



(a)



(b)

Fig. 5. Latex deposition at pH 9. Practically no latex is observed on the fiber surface due to the reversal of latex charge to negative (same as fibers).

Tensile Strength of Sheet

The results obtained at two levels of latex addition are presented in Figure 6. The dry and wet strengths of the sheet with and without heat treatment are recorded. Since control sheets without latex showed, independent of

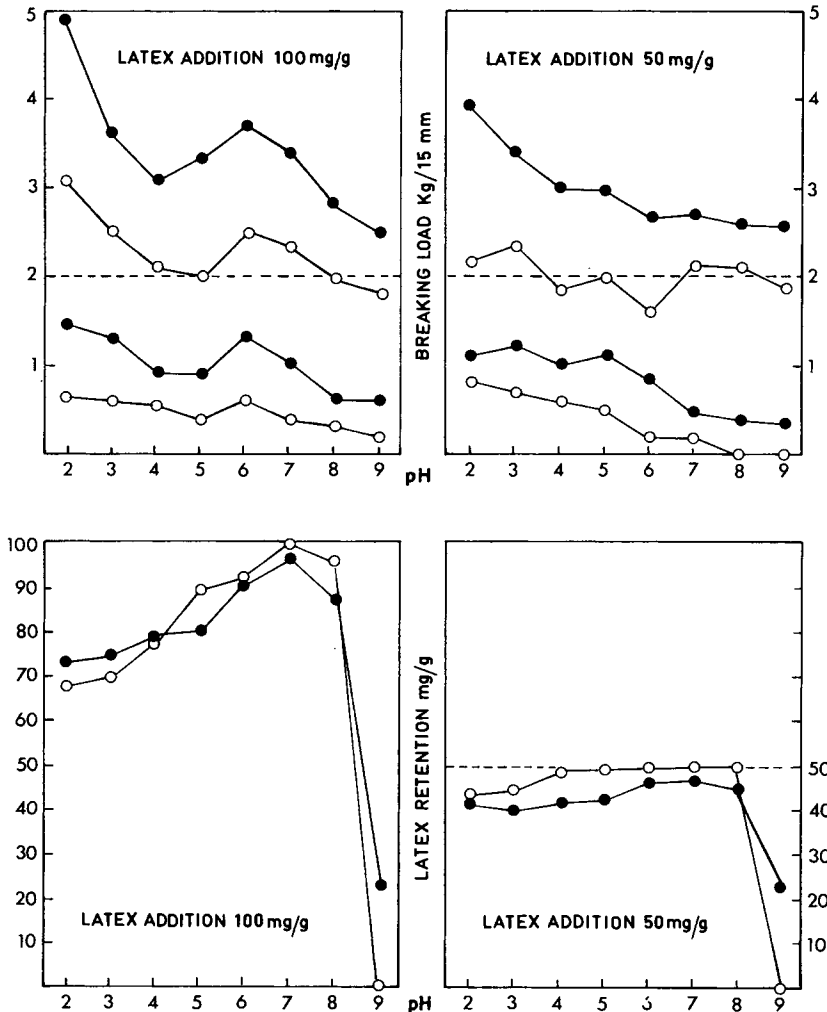


Fig. 6. *Upper:* Dry (upper two curves) and wet (lower two curves) breaking load of sheets formed from unbeaten kraft fibers treated with two levels of cationic latex. Additions are at various pH and the sheets are dried at room temperature (○) and subsequently at 105°C for 5 hr (●). Without latex, the dry strength is 2 kg (dashed line) and the wet strength is zero. *Lower:* Latex retention as a function of pH at two levels of addition determined in the fiber suspension (○) and in the formed sheet (●).

heat treatment, a dry strength of 2 kg and virtually no wet strength, it is seen that this latex generally improved the strength particularly after heating.

In general, the strength decreases with increasing pH. Departures from this general trend at 10% latex addition indicated by lower strength values at pH 3, 4, and 5 are attributed to the considerable flocculation and inferior sheet formation that was observed under these conditions.

The strength enhancement appears to be related to both the amount of latex retained in the sheet and to the uniformity of its distribution. In principle, the latex introduced into the sheet may influence the dry strength in various ways: (1) to replace the fiber-fiber bonding by forming an adhesive film between fibers in the region of their contact; (2) to supplement the inter-

fiber bonding by providing links between fibers outside their contact area; (3) to prevent the normal interfiber bonding that would otherwise be present in the absence of latex.

The results could be imagined to be a combination of these effects, and an increase or decrease in sheet strength depends on all of these and on the relative strengths of the interfiber bond and the bond with polymer interposition. Considering that the highest dry strength was achieved by uniform deposition of latex, it may be concluded that in this case the replacement of the fiber-fiber bonding is the most efficient. Deposition of latex as aggregates likely promotes supplementary bonding which, in view of our results, is less effective.

The development of wet strength can result from either the introduction of water-resistant links between fibers or a distribution of polymers which prevents water from penetrating to the interfiber bonds. The present experiments do not resolve these effects, but it is noteworthy that the measured wet strength was found to be independent of the presence or absence of the wetting agent.

The development of sheet strength with heat treatment results at least partly from changes in the latex which may be demonstrated with films formed by the latexes alone. Some of the strength development is attributed to the further gradual coalescence of the latex during which the boundaries of the coalescing particles disappear as polymer molecules from originally different particles interdiffuse.¹² The latexes may undergo further modification as oxidation and other effects related to the unsaturation of the butadiene occur. The films become stiffer and develop higher shear and tensile moduli.

Both effects improve the reinforcement of paper, and this may be seen most readily in the application of heat treatment. In Figure 6, the improvement of wet and dry strength by heat is apparent. Further effects of heat may be attributed to changes in the extent of the polymer-cellulose bond (spreading) or improvement in its quality. It is noted, however, that the trends attributed to latex distribution are not greatly altered by the heat treatment.

Support for the Suggested Effect of Latex Deposition

Supplementary experiments are illustrative of mechanisms involved in the sheet reinforcement by latex. The original latex deposited on fibers was hardened by bromination and thus prevented from coalescing, forming films, or establishing adhesive bonds and sheets were formed and tested. The results at 5% latex addition for both film-forming and hardened latex are shown in Figure 7. No wet strength is developed with the hard latex and the dry strength is less than the control and is sensitive to the pH of deposition. This is interpreted as resulting from the nonfilming latex interfering with the fiber-fiber bonding. The effect is greater as the distribution of latex is more uniform at low pH. With increasing pH, as latex aggregation permits more latex-free areas to be available for fiber contact, the effect decreases and the strength approaches that of the control. The results are thus consistent with, and reinforce, the predictions made on the basis of the electron micrographs.

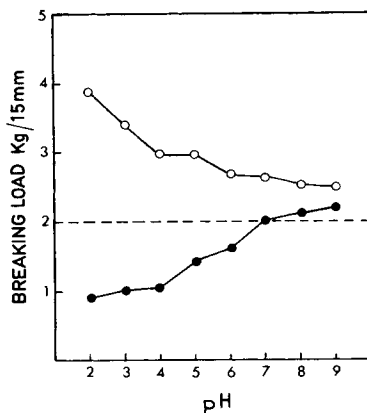


Fig. 7. Comparison of the breaking loads of sheets made with film-forming (○) or hardened (●) latex. The dashed line is for a control without latex. The sheets were heated at 105°C for 5 hr.

The properties of sheets containing the hardened latex were almost identical with and without heat treatment as a further consequence of bromination preventing film formation.

CONCLUDING REMARKS

The use of cationic latexes and the control of their deposition and distribution by pH provides a convenient model system for examining polymer-fiber relationships in composite sheet materials. One aspect of this relationship, the latex distribution, has been examined and the advantages of uniform distribution have been demonstrated for the polymers and fibers used.

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