On the mechanism of flocculation by microparticle retention-aid systems

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ABSTRACT

A microparticle retention-aid system (cationic polyacrylamide and anionic montmorillonite clay) was investigated using equipment designed to measure flocculation of cellulosic fibers. Comparison with a single-component system (cationic polyacrylamide) suggests that the flocculating efficiency of the dual-component system increases with increasing extension of the adsorbed polymer from the particle surface. This conclusion is supported by experiments that examined the binding of montmorillonite clay to fibers containing various levels of adsorbed cationic polyacrylamide. Another series of experiments showed that the efficiency of the microparticle system is enhanced by adding a low-molecular-mass polymer before adding the microparticle retention-aid system. The low-mass polymer functions as a site-blocking agent and maximizes extension of the retention-aid polymer.

Natural and synthetic polymers are often used to increase retention of pulp fines and added mineral fillers in the sheet. Conventional retention aids are not effective on high-speed paper machines, where high-shear forces tend to disrupt formed flocs. Retention aids designed for service in this environment must produce strong flocs that can withstand high shear. Most such retention aids are dual-component systems consisting of two oppositely charged polymers, which have a stronger flocculating ability than single-component systems *(1–6)*. In order to avoid the disturbance of anionically charged dissolved and colloidal material from the pulps, systems based on nonionic interactions have also been developed *(7–11)*.

The strong flocculating ability of these additives can cause problems, since sheet formation suffers if the degree of flocculation in the furnish is too high. Efforts to avoid this problem have led to yet another retention-aid concept, the so-called microparticle system. Such systems combine a cationic polymer with an anionic microparticle. Andersson *et al. (12)* combined a cationic starch with an anionic silica sol, while Lindström *et al. (13)* combined a cationic starch with an anionic precipitate of aluminum hydroxide. Langley and Litchfield *(14)* examined a system that combined a cationic polyacrylamide with an anionic montmorillonite particle. The general idea behind all of these systems is that the cationic polymer is added to the stock at an early stage so that the large-scale flocculation caused by this polymer can be broken down by shear forces. The anionic microparticle is then added shortly before the paper is formed.

Practical experience has shown that microparticle systems produce better formation. Indeed, Lindström has identified several benefits of microparticle systems *(15)*.

- When the flocculated suspension is exposed to high shear, significant reflocculation occurs when the shear rate is lowered.
- Dewatering in the wire section and the press section is more rapid.
- The dried paper sheet has a higher porosity.

Swerin *et al. (16)* were apparently the first to develop a detailed model of this kind of flocculant. It was found that microparticle systems are very efficient flocculants, producing a high degree of flocculation even at moderate floc sizes. On the other hand, a microparticle system required a larger polymer dosage than a comparable single-component retention-aid system to achieve maximum flocculation. The research also showed that flocs formed by the microparticle retention aids could be re-formed and that the reflocculated flocs were smaller and denser. Finally, there was the interesting discovery that microparticle systems were less sensitive to overdosing than single-component retention-aid systems, especially for polymers with a high- charge density.

The present study was undertaken to extend the research of Swerin *et al. (16)* in an effort to further clarify the flocculation mechanism of microparticle retention-aid systems.

EXPERIMENTAL

Materials

Pulp. Cellulosic fibers were obtained from a fully bleached kraft softwood pulp collected at the Östrand mill (SCA Graphic Sundsvall AB, Sundsvall, Sweden) in a dry-lap form. Before further use, the pulp was disintegrated according to the standard procedure described in SCAN C18.

Retention aids. A cationic polyacrylamide copolymer (Allied Colloids Ltd., Bradford, U.K.) consisting of acrylamide and N,N-dimethyl-

aminoethyl acrylate quaternized with methyl chloride was used as one component in the microparticle retention-aid system. The same polymer was also used as a single-component retention aid in parallel experiments that served as a reference for evaluating the microparticle system. The weight average molecular mass of this polymer was determined to be 5.8 x 10^6 using a GPC (gel-permeation chromatography) method described in the literature *(17)*. The charge density of the polymer was determined to be 1.8 meq/g by polyelectrolyte titration. This polyacrylamide copolymer was used without further purification. A fresh polymer solution was prepared every day to avoid disturbances from changes in the solution properties of the polymer. A detailed description of the preparation of the polymer solution is given in the literature *(16)*.

The second component of the microparticle system was a montmorillonite clay that was swollen overnight in deionized water before use. In one set of experiments, the adsorption of bentonite to polymer-presaturated cellulosic fibers was measured. For these experiments, the montmorillonite solution was centrifuged, and only the supernatant was used to measure bentonite adsorption.

Polydimethyl diallyl ammonium chloride (polyDMDAAC) with a molecular mass of 1.2 x 10^6 and a charge density of 6.19 meq/g was used in one experimental series. Molecular mass was measured by GPC *(17)*, and charge density was determined by polyelectrolyte titration. This polymer was also supplied by Allied Colloids, and the low-molecular-mass material of this polymer was removed according to a procedure described in the literature *(18)*.

Other materials. In the polyelectrolyte titrations, an anionic polymer, potassium polyvinyl sulfate (Wako Pure Chemicals, Japan), was used together with a cationic indicator, orthotoluidine blue (Kebo AB, Sweden). Both compounds were delivered as powders and were used without further purification.

The water used in the flocculation experiments was tap water, whereas the water used in all other experiments was deionized water.

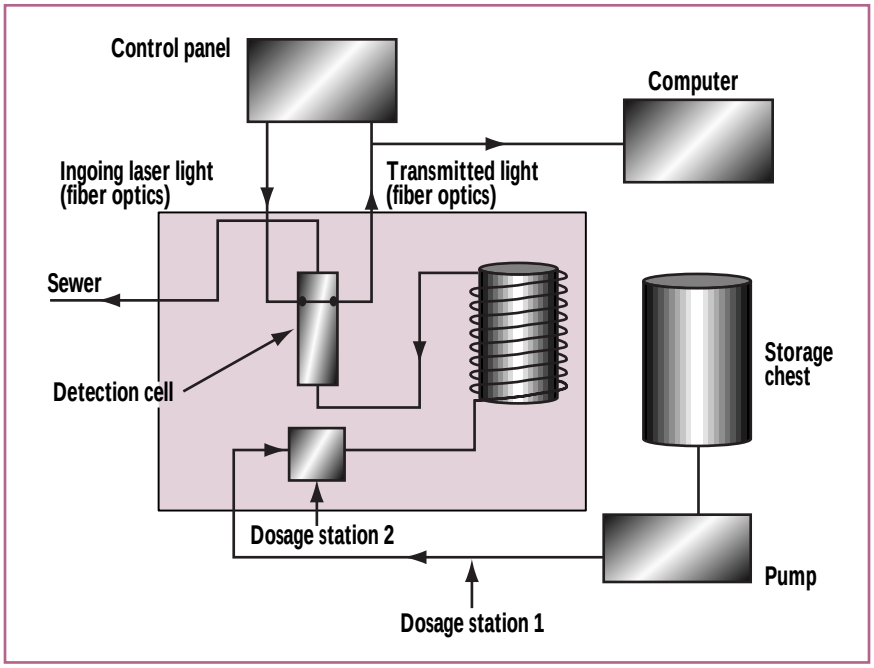
Inorganic electrolytes used throughout the experiments were of analytical grade.

Methods

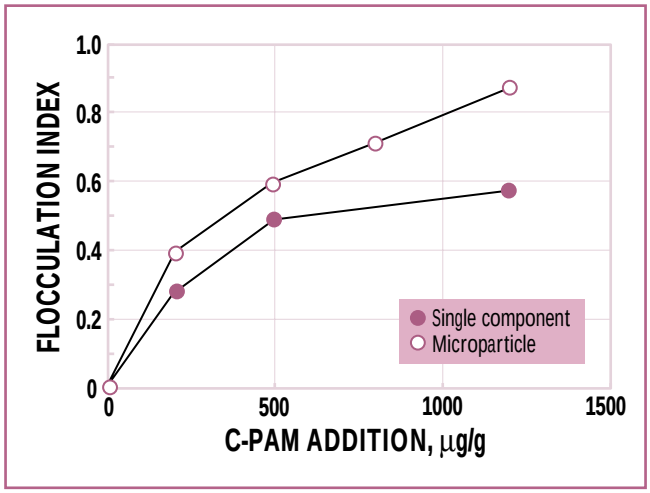
Fiber preparation. After reslushing, the fibers were washed at both high and low pH to remove most of the remaining adsorbed metal ions, counterions to the charged groups on the fibers, and dissolved and colloidal material. The procedure is described in the literature *(19)*.

Polymer adsorption. General. The cationic polyacrylamide (C-PAM) and polyDMDAAC polymers were adsorbed onto cellulosic fibers at pH 8 at room temperature and at a fiber concentration of 5 g/L. Before the adsorption measurements, the fibers were converted to their sodium form by excessive washing at pH 8. The adsorption time for the C-PAM was 2 min, while the adsorption times for polyDMDAAC was 10 min. This was done to match the times in the flocculation experiments, as explained later. Excess polymer in solution was measured by polyelectrolyte titration using an anionic polymer, potassium polyvinyl sulfate, and orthotoluidine blue as an indicator. The procedures for titration are described in the literature *(20, 21)*.

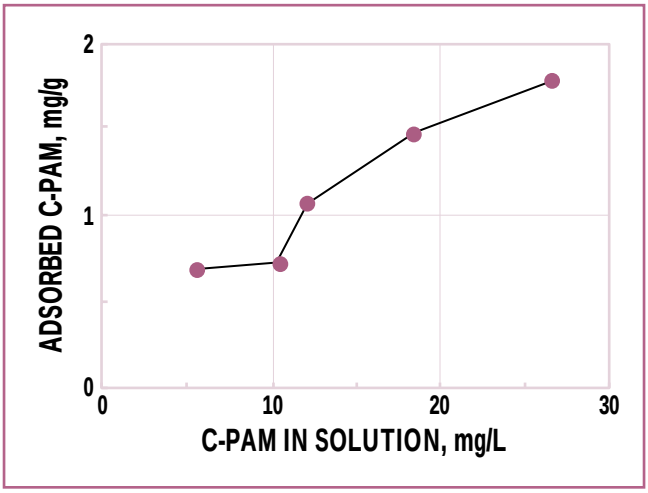
Presaturation of fibers with C-PAM. One set of experiments involved measuring montmorillonite adsorption onto fibers that had been presaturated with C-PAM. The polymer was added to the fibers at a concentration of 2 g/L and allowed to adsorb for 3 min. The water was then removed by filtration on a Büchner funnel fitted with a Munktell No. 3 filter paper (Kebo AB, Sweden). An extra 50 mL of water was added to the filtered fiber suspension to displace any excess polymer



1. Schematic of fiber-optic flocculation sensor equipment



2. Flocculation of cellulosic fibers, measured as flocculation index, for the single-component system and the microparticle system (fiber concentration = 2 g/L; montmorillonite addition = 2 mg/g fiber)



3. Adsorption of C-PAM on cellulosic fibers (fiber concentration = 5 g/L; contact time between fibers and polymer = 2 min)

that might be present in the filter cake. The fibers were then redispersed to a concentration of 20 g/L, and the montmorillonite was added and allowed to adsorb for 5 min. Excess montmorillonite in solution was determined using ICP–AES (inductively coupled plasma–atomic emission spectroscopy) analysis (Thermo Jarel Ash, U.K.) of the water phase. The iron concentration measured in this procedure was used to establish a calibration curve of the montmorillonite concentration.

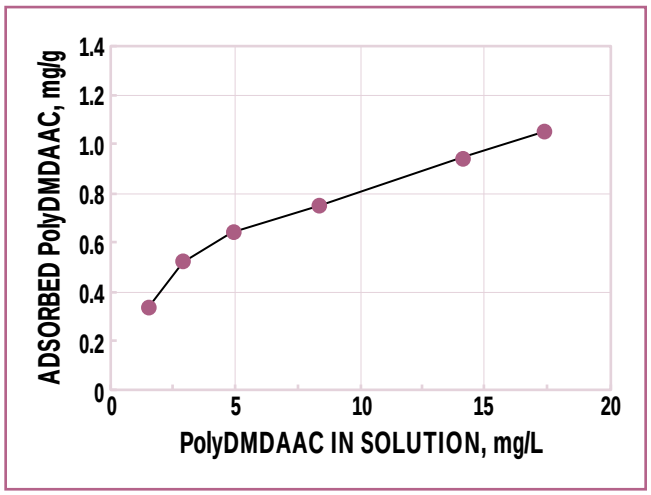
Preadsorption of fibers with polyDMDAAC. Another set of experiments was carried out to determine how preadsorption of polyDMDAAC affected subsequent adsorption of C-PAM onto the fibers. The polyDMDAAC was preadsorbed on the fibers for 10 min. After a washing step, C-PAM was applied to a slurry with a fiber concentration of 5 g/L and allowed to adsorb for 2 min. Adsorption of C-PAM onto the precovered fibers was measured using polyelectrolyte titration.

Measurement of fiber flocculation. A modified version of the fiber-optical flocculation sensor was used to measure the polymer-induced fiber flocculation *(22, 23)*. Figure 1 is a schematic representation of the equipment.

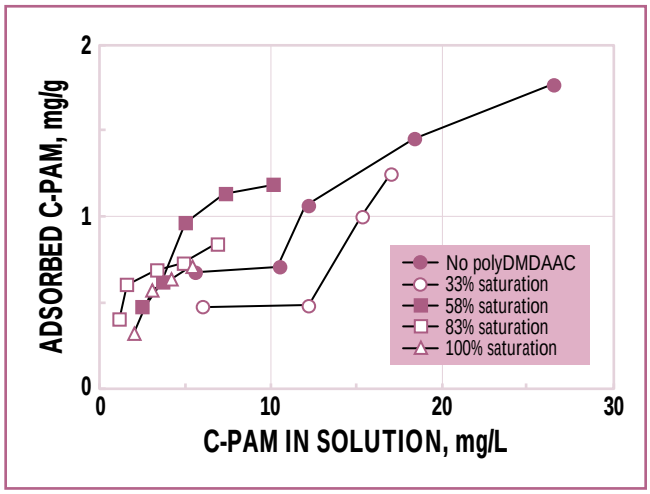
In principle, a fiber slurry at a concentration of 2 g/L is pumped from the storage chest through the detection cell. Chemicals can be added at three different positions in the system. First, they can be added in the storage chest, with a minimum residence time from the storage chest to the detection cell of 10 min. When polyDMDAAC was used, this chemical was always added to the storage chest. C-PAM was added at dosage station 1. From this position, it takes approximately 2.5 min for the slurry to reach the detection cell. The C-PAM was pumped into the slurry at a controlled rate and thoroughly mixed with the fibers in a closed beaker fitted with a magnetic stirrer. At the last addition point—dosage station 2—the montmorillonite was pumped into the fiber suspension at a controlled rate and mixed with the fibers in a specially constructed mixing chamber where the polymer solution and the fiber mixture are introduced at a 90° angle to each other. The delay time from dosage station 2 to the detection cell was approximately 1.5 min. The plungers used for the addition of C-PAM and montmorillonite were of the Perfusor Secura type (B. Braun Melsungen AG, Germany).

Flocculation was evaluated by methods described in detail in the literature *(5, 24)*. In principle, the dimensions of the formed flocs are measured by passing a laser beam through the detection cell. The transmitted light is collected by fiber optics and transferred to a phototransistor. The signal from the phototransistor is then subjected to a frequency analysis, and a frequency power spectrum of the signal is calculated. The frequency power spectrum is then converted to a wavelength power spectrum by normalizing with respect to the average velocity of the suspension in the measuring zone, 0.8 m/s in all experiments. The coefficients of variation of the signal with and without the addition of polymer (V_2 and V_1, respectively) were then used to calculate the flocculation index, FI, according to Eq. 1.

$$FI = (V_2^2 - V_1^2)^{1/2}/V_1 \qquad (1)$$



4. Adsorption of polyDMDAAC on cellulosic fibers (fiber concentration = 5 g/L; contact time between fibers and polymer = 10 min)



5. Adsorption of C-PAM on cellulosic fibers precovered to different degrees with polyDMDAAC, given as a percentage of the plateau level of adsorption of polyDMDAAC (fiber concentration = 5 g/L; contact time between fibers and polymer was 10 min for polyDMDAAC and 2 min for C-PAM)

The flocculation index is thus a measure of the degree of flocculation of the fiber suspension.

When polyDMDAAC was added before the C-PAM, it caused a flocculation with the added montmorillonite by itself. To determine the extent of the flocculation caused by the C-PAM, the value of V_1 used in Eq. 1 was the coefficient of variation of the signal for the suspension containing added montmorillonite and polyDMDAAC, while the V_2 value corresponded to the situation when all three components had been added.

When the adsorption times in the polymer adsorption part of this investigation and the residence times in the flocculation experiments are compared, it is obvious that there are some differences. These differences are due to experimental difficulties encountered when trying to use the same times in the adsorption measurements as in the flocculation measurements. All adsorption and flocculation measurements were conducted at pH 8.

RESULTS AND DISCUSSION

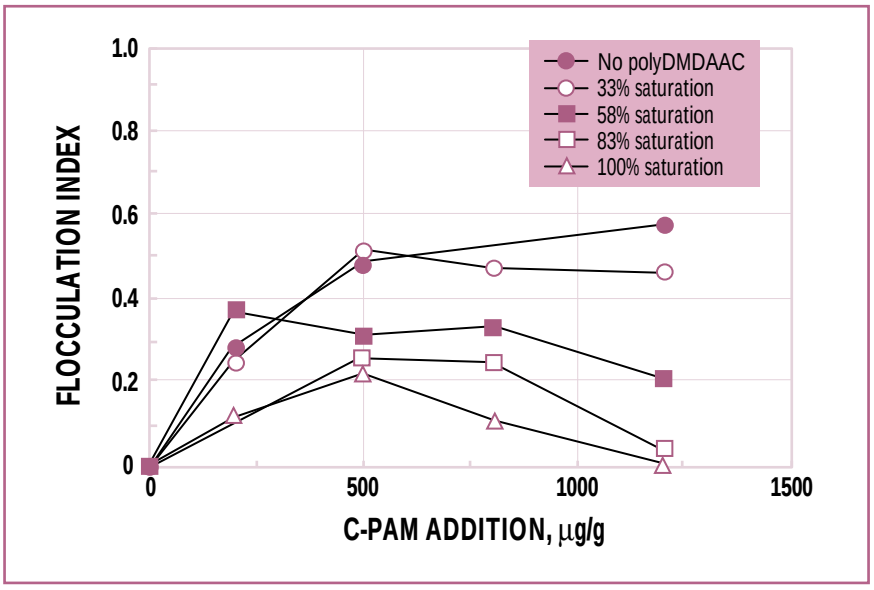
Correlation between flocculation and polymer adsorption

Comparison of microparticle and single-component systems. The performance of a microparticle-based retention-aid system was compared with that of a single-component retention-aid system. A cationic polyacrylamide (C-PAM) was tested with and without the microparticle in the equipment designed to detect flocculation (Fig. 1). The C-PAM was added at dosage station 1. The montmorillonite portion of the microparticle system was added at dosage station 2.

The results in Fig. 2 show that the two systems are fairly comparable at low levels of polymer addition (<500 µg/g). The flocculation index for the microparticle system is substantially higher at higher levels of polymer addition. The single-component system closely follows the typical behavior of a bridging flocculant *(25)*. To investigate this behavior in greater detail, experiments were carried out to develop an adsorption isotherm for the C-PAM on the fibers. The shape of the isotherm in Fig. 3 does not show a high-affinity behavior. There are several possible explanations for this behavior:

1. Polydispersity of the polymer
2. Kinetic effects from the rearrangements of the polymer on the surface at these short adsorption times (2 min), as discussed in the literature *(26, 27)*
3. Changes in the conformation of the polymer because of changes in concentration of polymer in solution
4. An uneven charge distribution within one polymer molecule and between different molecules.

Since the concentration during the adsorption measurements was low and the contact time was very short, it is believed that the second item is the most probable explanation for the shape of the isotherm. Nevertheless, the concentrations and adsorption times used to obtain this isotherm are very relevant to what is happening during the flocculation measurements. As can be seen in Figs. 2 and 3, polymer addition of



6. Flocculation of cellulosic fibers, measured as flocculation index, caused by the single-component system at different levels of precoverage of the fibers by the polyDMDAAC used as a site-blocking agent, given as a percentage of the plateau level of adsorption of the polyDMDAAC (polymer added was C-PAM; fiber concentration = 2 g/L)

500–1000 μg/g is very close to a 50% surface coverage of the fibers, which is close to what is theoretically predicted as an optimum surface coverage for bridging flocculation *(25)*. This is under the assumption that the adsorption is very fast, which is strongly supported by the results of Falk *et al. (28)*.

Probable role of polymer conformation. The results for the microparticle system do not fit this discussion unless it is assumed that the system works through bridging of the montmorillonite particles between strands of adsorbed polymer molecules on adjacent fibers. If this is assumed, it could be argued that it would be advantageous if the surface coverage of C-PAM on the fibers were as high as possible. This would produce a large extension of the polymer molecules out from the surface, which would in turn promote a large interaction between the polymer and the montmorillonite particles. This also emphasizes the fact that the conformation of the polymer on the surface of the fibers is not taken into account in the bridging model *(25)*. However, later work *(29)* has shown that polymer conformation is very important for the single-component system and even more so for the microparticle system.

If this hypothesis is correct, it could explain the similarity of the systems at lower levels of polymer addition, where the reconformation of the polymers can take place. At higher levels of addition, the microparticle system can benefit from the more extended conformation of the polymer, whereas the flocculation efficiency for the single-component system starts to level off as the fiber surface approaches saturation (surface coverage >50%). This general discussion is also supported by the results of earlier work *(30)*, which showed that the thickness of the adsorbed layer of C-PAM (similar to the polymer used in the present investigation) on silica increased at low levels of polymer adsorption. This is in contrast to the situation for uncharged polyethyleneoxide, where the layer thickness increased mostly close to the saturation adsorption *(31)*. The reason for this difference between copolymers and homopolymers is probably that only the charged blocks of the copolymer are adsorbed on the silica surface.

Testing the role of polymer conformation—effect of adding a site-blocking agent. To test this general hypothesis, the fiber surfaces were blocked by preadsorbing a cationic polymer of lower molecular mass (polyDMDAAC), thus preventing the C-PAM from reconforming at lower levels of addition. This is very close to the site-blocking-agent concept introduced by Behl *et al. (32)*, but the reason for introducing polyDMDAAC is quite different. To determine the level of addition of the site-blocking polyDMDAAC polymer, it was necessary to measure its adsorption on the fibers.

The isotherm in Fig. 4 shows the results of these experiments. The saturation level was chosen as 0.5 mg/g by extrapolating the isotherm to zero polymer concentration in solution. Fiber surfaces were precovered to five different levels of saturation (zero, 33%, 58%, 83%, and 100%) by adding polyDMDAAC. The fibers were then washed, and C-PAM was added. The five corresponding adsorption isotherms for C-PAM on the pretreated fibers are shown in Fig. 5.

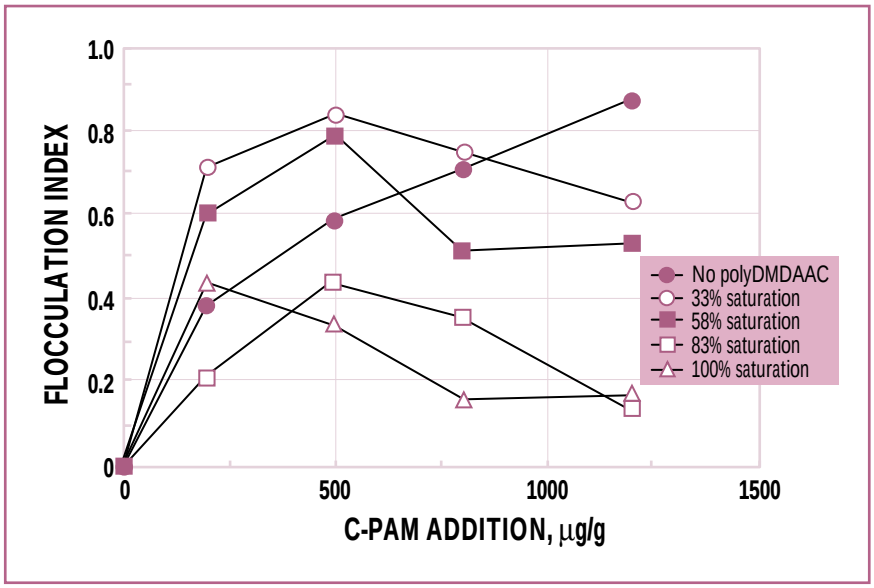
The curves for zero and 33% precoverage have the same general shape, probably because of the nonequilibrium conditions used in the experiments, as discussed previously. It can also be seen that the level of C-PAM adsorption is lower for the fibers precovered to 33%. The rest of the isotherms also show that increasing the amount of polyDMDAAC reduces the adsorption of polymer, as expected. However, it is also clear that it is difficult to obtain a stoichiometric exchange of the C-PAM for the polyDMDAAC from

these results. Even at 100% precoverage, it is still possible to adsorb a significant amount of C-PAM. There can be several reasons for this, but considering the shape of the adsorption isotherm for the polyDMDAAC, it is clear that increasing the addition of polymer leads to increased adsorption. It therefore is logical to assume that C-PAM can be adsorbed on the presaturated surface. The C-PAM can adsorb either by desorption of the polyDMDAAC or, more probably, through a reconformation of the polyDMDAAC, i.e., desorption of segments of the polymer. Further experiments are needed to determine the mechanism behind this, but the important result for the present investigation is that it is possible to affect the adsorption of the C-PAM by adding a site-blocking agent.

The main reasons for introducing a site-blocking agent were (a) to test the hypothesis that the conformation of the C-PAM was important and (b) to determine the effect that polymer conformation might have on the flocculation efficiency of a single-component system and a microparticle system.

The results for the single-component system in Fig. 6 show that the addition of the site-blocking agent decreased the flocculation efficiency while shifting the maximum in the flocculation curves to lower levels of polymer addition. This is in accordance with the general concepts of the bridging theory *(25)*. When maximum adsorption of C-PAM decreases, the number of polymer molecules at maximum flocculation, i.e., at a surface coverage of 50%, also decreases, and the flocculation efficiency of the polymer should therefore decrease. This is indeed evident in Fig. 6.

The results for the microparticle system at different levels of fiber precoverage with the site-blocking agent are shown in Fig. 7. In general, the results are quite different from

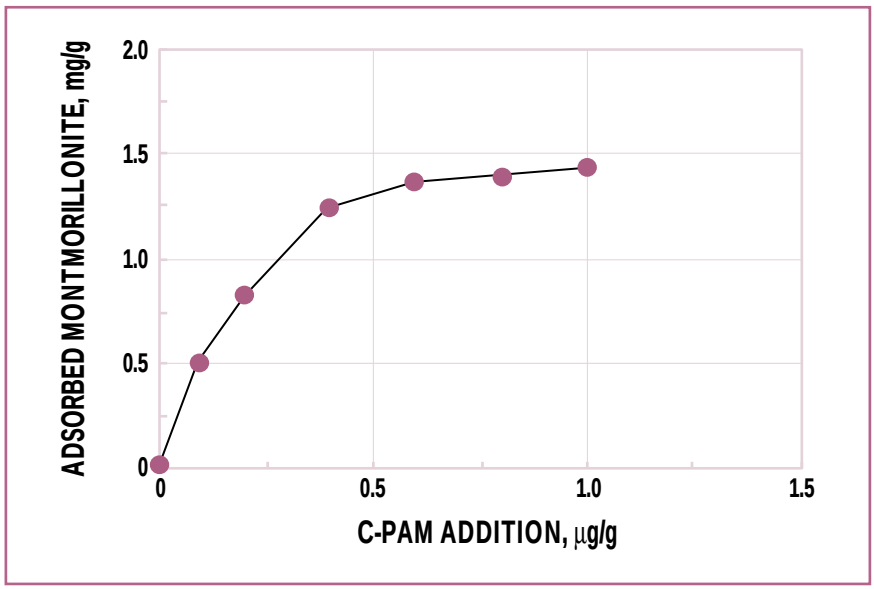


7. Flocculation of cellulosic fibers, measured as flocculation index, caused by the microparticle system at different levels of precoverage of the fibers with polyDMDAAC, given as a percentage of the plateau level of adsorption of the polyDMDAAC (polymer added was C-PAM; montmorillonite addition = 2 mg/g fiber; fiber concentration = 2 g/L)

those achieved with the single-component system. The efficiency of the microparticle system is significantly increased at lower levels of precoverage (33% and 58%). This again indicates that the addition of the site-blocking agent increases the outward extension of the cationic polymer from the fiber surface. The extended conformation significantly increases the polymer's interaction with the added microparticles, thus increasing its efficiency. At higher levels of precoverage, the number of polymer linkages naturally decreases because of the reduced adsorption of the C-PAM. This can be seen in Fig. 5, where a change in precoverage from 58% to 83% reduced adsorption of C-PAM from 1.2 mg/g to 0.7–0.8 mg/g. Obviously, the amount of precoverage is critical to the efficiency of the system. A theoretical discussion of how presaturation with a site-blocking polymer affects the microparticle system is available in the literature *(29)*.

When polyDMDAAC was used as a site-blocking agent, the flocculation index achieved a maximum and then declined with added levels of C-PAM. The most likely explanation for this behavior is that the fibers have no more sites capable of adsorbing C-PAM at higher levels of polymer addition. The unadsorbed C-PAM probably forms complexes with the montmorillonite. It has been shown that formation of such complexes is less efficient than that between polymers preadsorbed on the fibers *(5)*. However, it should be possible to overcome this problem by adding more montmorillonite at higher levels of C-PAM addition, since the C-PAM molecules that have been adsorbed on the fibers should still be available for adsorption after the unadsorbed C-PAM has formed complexes with the added montmorillonite.

Further experiments are needed to test this hypothesis further, but the present results support the idea that the efficiency of the investigated microparticle system is due to a linkage of the montmorillonite particles by strands of polymer segments



8. Adsorption of montmorillonite on cellulosic fibers precovered with C-PAM (C-PAM preadsorption time = 3 min, fiber concentration = 2 g/L; montmorillonite addition = 2 mg/g fiber, adsorption time = 5 min, fiber concentration = 20 g/L)

adsorbed on adjacent fibers. In real systems, it is possible that this microparticle linkage can be formed between polymers adsorbed on fibers and filler particles. Nevertheless, an extended conformation of the polymer out from the fiber surface seems to be very important in achieving the full potential of the added chemicals. It might also be added that Hoffman's recent work *(33)*, which was published long after the experiments in the present investigation were conducted, discusses the concept of microparticle bridging between particles with preadsorbed polymers. However, Hoffman does not address the issue of polymer extension from the fiber surface *(33)*.

Adsorption of montmorillonite on fibers precovered with C-PAM

Much of the previous discussion has focused on the interaction between polymers on the fiber surfaces and montmorillonite particles in the solution. It was therefore important to measure the adsorption of montmorillonite. This was done by pretreating the fibers with C-PAM, removing excess C-PAM, and then exposing the fibers to a solution of montmorillonite.

The results for montmorillonite adsorption are presented in Fig. 8. Since the level of polymer addition was very low in these experiments, it was not possible to measure the adsorption of C-PAM by polyelectrolyte titration. Therefore, the results in Fig. 8 are based on the amount of polymer added instead of the adsorbed amount of polymer.

Figure 8 shows that montmorillonite adsorption increased rapidly with increasing levels of C-PAM addition. This agrees with the results of Wang and Audebert *(30)*, who showed that the adsorbed layers of copolymers of cationic polyacrylamides on silica particles increased their thickness in the same way as the adsorption in Fig. 8. Wang and Audebert claimed that the increase in thickness was due to the fact that only the charged segments were adsorbed, whereas the nonionic segments could still protrude into solution. Since nonionic polyacrylamide can adsorb on montmorillonite *(11)*, it might be suggested that the binding of the montmorillonite to fibers precovered with C-PAM may be due to an interaction between the noncharged segments and the mineral particle. This should be critically tested in future experiments where, for example, the influence of the degree of substitution of the C-PAM should be considered.

It is also interesting to note the close similarity between the change in the slope in the flocculation experiments at 500 μg/g (Fig. 7) and the leveling off of the adsorption of montmorillonite (Fig. 8). These results suggest that flocculation in the microparticle-based system is caused by the interaction between preadsorbed polymers (on adjacent fibers) and montmorillonite particles. This would also explain the high degree of reflocculation of these systems, as noted by Lindström *(15)*. Given the large surface coverage at maximum efficiency of the microparticle system, it is reasonable to conclude that floc disruption will not necessarily reduce polymer extension.

Figure 7 also shows that the flocculation index increased even at polymer additions >500 μg/g, despite the fact that no more montmorillonite is adsorbed to the fibers above this level of polymer addition. The reason for this is not obvious, but there is probably a change in the fraction of C-PAM covered by the montmorillonite particles, since the amount of adsorbed C-PAM increases at higher addition levels, and this might enhance the flocculation efficiency *(29)*. It is not clear why montmorillonite adsorption does not increase at the higher levels of C-PAM addition, and this should also be clarified in future experiments.

CONCLUSIONS

The mechanism behind microparticle-based flocculants involves a

KEYWORDS
Acrylamide, acrylic compounds, addition polymers, amides, anionic compounds, bibliographies, cationic compounds, clay, fibers, flocculation, minerals, montmorillonite, polyacrylics, reaction mechanisms, retention aids, synthetic polymers, thermoplastics, vinyl compounds.

bridging of the montmorillonite particles between strands of adsorbed polymer molecules on adjacent fibers. This conclusion is supported by

- Flocculation experiments, where the conformation of the adsorbed C-PAM was altered by a site-blocking polymer, which served to increase the extension of the polymer from the fiber surface
- Adsorption experiments, where the binding of montmorillonite to fibers precovered with C-PAM was measured.

The flocculation experiments showed that addition of a site-blocking agent strongly improved the efficiency of the microparticle system. The same site-blocking agent reduced the efficiency of a single-component C-PAM system. These results are consistent with theories for bridging flocculation.

The amount of C-PAM required to reach maximum efficiency was higher for the microparticle system. This is probably because the microparticle system needs a fully extended polymer conformation to achieve its full potential. Once this conformation is achieved, the polymer does not reconform, even when the flocs are broken down. This would also explain why microparticle systems tend to reflocculate after the flocs have been severely sheared.

The adsorption experiments show that much remains to be learned about the polymer adsorption at short contact times and different fiber concentrations. TJ

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