Highly branched cationic polyelectrolytes: Fines retention

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ABSTRACT

Highly branched cationic polyacrylamide (HBC-PAM) has been investigated as a retention aid for microparticulate retention systems. The investigation reveals that the HBC-PAM provides higher first-pass fines retention (FPFR) than linear polymers when the papermaking stock is exposed to high shear conditions. Also, as a retention aid, the HBC-PAM is superior to corresponding linear polymers for spherical colloidal silica but is inferior for plate-like bentonite.

Application:

The HBC-PAM has significant potential for microparticle retention systems, which allow a greater degree of freedom in selecting the addition point for this polymer

RETENTION HAS BEEN RECOGnized for many years as one of the most important aspects of papermaking. Careful application of retention aids allows many benefits, such as optimized wet-end running conditions, improved paper properties, maximized raw material yield, and reduced effluent load.

Since the importance of colloidal flocculation in retention has been known to the papermaking industry *(1, 2),* various polyelectrolytes *(3)* have been developed and widely used as retention aids for several decades. It was common practice to apply a single polyelectrolyte to a papermaking system as a retention aid. Simplicity and relatively high flocculation efficiency are major reasons for the long-term application of this single polyelectrolyte retention system. However, it has been recognized that this simple retention system lacks retention power under highly turbulent conditions. To obtain high retention of fines on high-speed paper machines, dual-polymer *(4–6)* or microparticle retention systems *(7, 8)* have been developed and widely adopted. Since two linear polyelectrolytes are generally used in a dual retention system, it is common to produce papers with bad formation due to overflocculation when trying to increase the retention of fines. By using microparticle retention systems, this problem may be avoided. However, microparticle systems restrict the addition point of polymers for best performance.

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As described in previous papers *(9, 10),* the floc that is formed with a highly branched cationic polyacrylamide (HBC-PAM) is peculiar in terms of its tenacity and size. This polymer may have great potential as a papermaking retention aid. Since it tends to produce flocs with relatively small size and has a high tenacity against shear, very little attention may be required in applying this as a retention aid. The HBC-PAM is applied in a microparticulate retention system as a polyelectrolyte. First-pass retention of fines is measured, and the results are compared with those of conventional retention systems.

EXPERIMENTAL

Highly branched cationic polyelectrolytes based on acrylamide (HBC-PAMs) were polymerized as described in a previous paper *(9).* Nonionic (N-PAM) and cationic linear polyacrylamides (C-PAMs) were also polymerized for comparison. These different types of polymers were applied to currently used microparticulate retention systems *(7, 8)* such as the Hydrocol and Compozil retention programs. Polyelectrolytes and other materials used in this work are listed in **Table I.**

Papermaking stock, containing 1.75 g of hardwood bleached kraft pulp (HwBKP) refined to 400 mL CSF and 0.75 g of ground calcium carbonate (GCC), was placed into a dynamic drainage jar (DDJ) *(11, 12)* with a 200-mesh screen; the jar was filled with water to achieve a total volume of 500 mL. After stirring the stock at 750 rpm for 3 min, polymers followed by inorganic microparticles were added to the DDJ. Then 10 mL of the first drained effluent was discarded, and 100 mL of the second was taken out. The second drained effluent was filtered, and the weight of the filtered solid was determined by gravimetry as a first-pass fines retention (FPFR). The slurry of pulp and GCC without polymers and microparticles was drained until the filtrate became clear. The weight of the total drained solid was taken as a fines fraction. The FPFR was calculated as a percentage of the fines fraction according to TAPPI Test Method T 261 cm-94.

The zeta potential was determined by using a Mobility Meter II (Paper Chem. Lab. Inc.). Cationic charge densities of the polymers were determined by a colloid titration method. In this measurement, potassium salt of polyvinylsulfate (PVSK, MW = 2000) and toluidine blue were used as a titrant and an indicator, respectively *(13).* Charge Analyzer II (Rank Brothers, UK) was also used in determining the cationic charge density of polyelectrolytes. The concentrations

Materials	Type of materials	Remarks
N-PAM	Linear	Nonionic linear polyacrylamide
C-PAM1	Linear	Cationic linear polyacrylamide
C-PAM2	Linear	Cationic linear polyacrylamide
C-Starch	Branched	Cationic starch
HBC-PAM	Highly branched	Highly branched cationic polyelectrolyte based on acrylamide
Colloidal silica	Spherical	Microparticles used in Hydrocol[a] retention program
Bentonite	Plate-like	Microparticles used in Compozil[b]

[a]Retention program of Allied Colloids Ltd., U.K.
[b]Retention program of Eka-Nobel Ltd., Sweden

I. List of materials used in this experiment

Polyelectrolyte	Viscosity at 25°C, cp*	Charge density at pH 4.5, meq/g
N-PAM	820	–0.3
C-PAM1	1080	1.9
C-PAM2	640	1.8
C-Starch	100	0.4
HBC-PAM	330	1.6

*Polymer viscosities were determined by using a Brookfield viscometer (RV, No. 4 spindle) at 1.0 wt.% polymer solutions.

II. Viscosity and charge density of polyelectrolytes used in this experiment

of titrant and titrated polymers were 1/400N and 0.001 wt.%, respectively. The titrant was added very slowly to ensure complete reaction. The titrant was added for 30 min in a typical titration.

Handsheets were prepared and the physical properties were measured as described in TAPPI Test Methods. Formation data of the handsheets were obtained from a Reed nonuniformity index (NUI) meter (MK II, Noram, PQ, Canada).

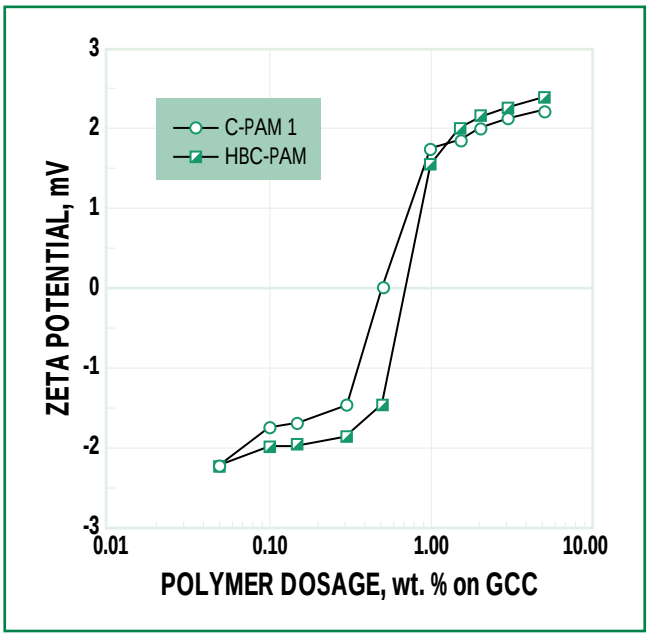
RESULTS AND DISCUSSION

Figure 1 shows the zeta potential of GCC as a function of polymer concentration. The concentrations of cationic linear polyacrylamide (C-PAM1) and HBC-PAM required to reach the isolectric points were about 0.5 and 0.7%, respectively, indicating that the cationic charge density of C-PAM1 is slightly higher than that of HBC-PAM. The viscosity and charge density of polyelectrolytes used in this work are listed in **Table II**. A charge complexation method was used to measure charge densities of linear polymers. Complexation between positive charges in the polymer and anions in the titrant might be affected by the structures of polymers. However, every cation in the polymer may not react with the anion in the titrant. Some of cations would be buried, and these cations would remain unreacted throughout the titration. The fraction of buried cations might be higher in highly branched polymers than in linear polymers. To minimize the inaccuracy caused by this effect, titration was carried out using dilute solutions and a titrant that has a much lower molecular weight than the polymer being titrated. The detailed procedure is described in "Experimental."

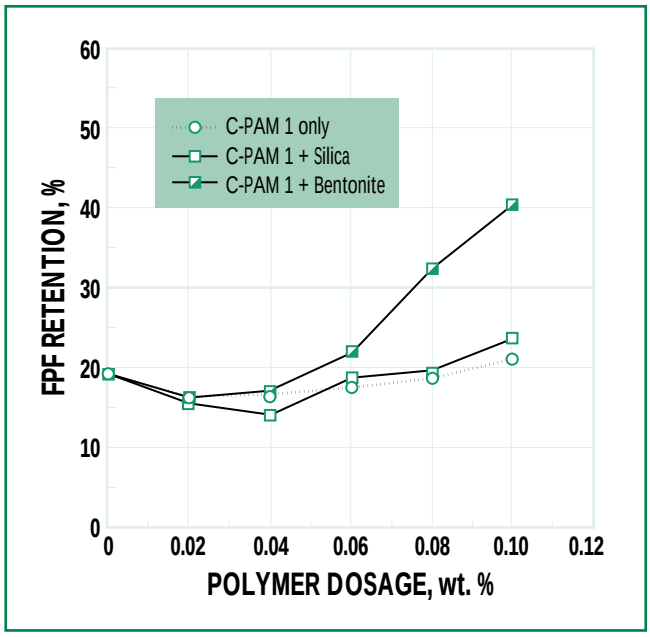
Figures 2 and 3 show that first-pass retention of fines (FPFR) increases with the polymer dosage. These figures show that incorporation of microparticles into the retention system significantly improves FPFR. In the case of linear C-PAM1, the use of bentonite rather than colloidal silica shows greater retention efficiency. On the other hand, better retention of fines is achieved when spherical colloidal silica is used as a microparticulate retention additive for HBC-PAM. The combination of HBC-PAM and colloidal silica evidently outperforms that of the C-PAM1 and bentonite in retention. It can be concluded from the results that a proper combination of polymer shapes with typical microparticles is required to obtain a better retention efficiency in a microparticulate retention system.

The effect of the types of polyelectrolytes and microparticles on FPFR is also determined by using a DDJ. To a papermaking stock containing fiber, fiber fines, and GCC (30 wt.%), 0.1 wt.% of the polymer is added; this is then followed by adding either 0.2 wt.% of bentonite or silica. When linear polyelectrolytes such as N-PAM, C-PAM1, and C-PAM2 are used as retention aids, bentonite is applied. Colloidal silica is used as a microparticle when highly and moderately branched polyelectrolytes such as HBC-PAM and cationic starch, respectively, are used as retention aids. The branched polymers show better retention efficiency than the linear polyelectrolytes, as shown in **Fig. 4**, indicating that the three-dimensional branched structure of these polymers tends to promote fines flocculation. Note that the flocs formed with HBC-PAM are smaller than those formed with linear C-PAM1, and the average floc size flocculated with HBC-PAM and colloidal silica is approximately 10 μm, as described in our previous paper *(9)*. However, this relatively small floc size is enough to obtain good fines retention. This suggests that a large floc size formed by electrostatic force is not necessary in retention.

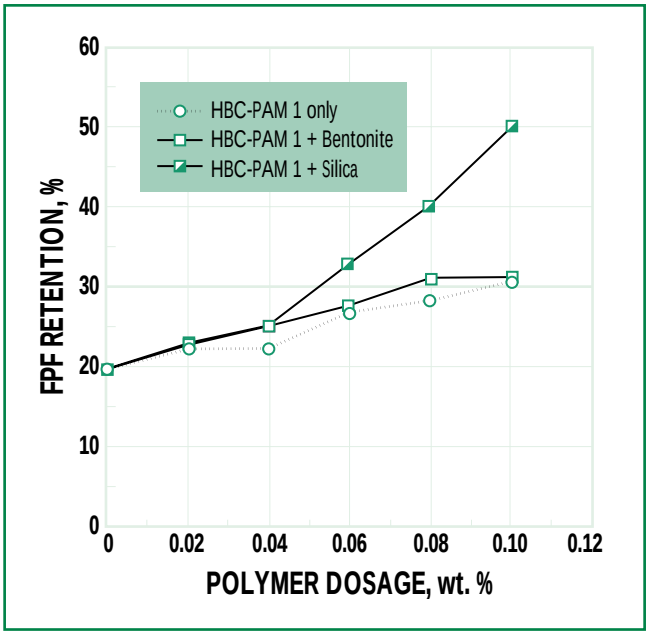
The dependence of FPFR on the agitation speed of the DDJ is shown in **Fig. 5.** When the agitation speed is



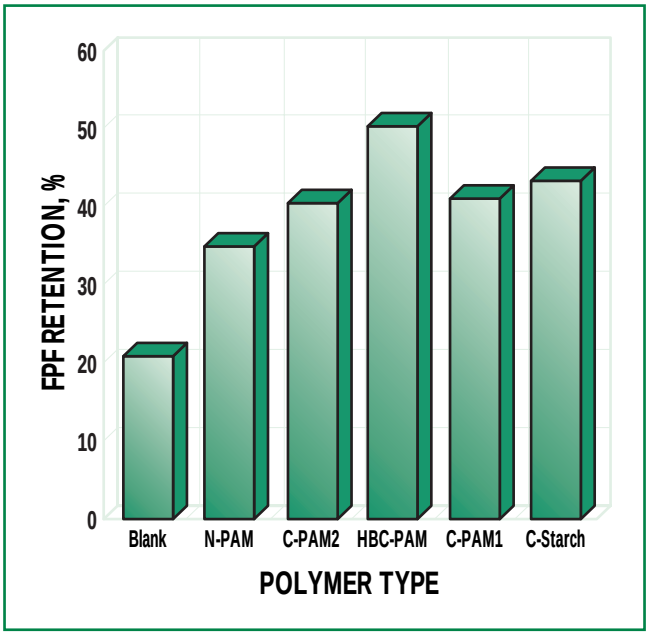
1. Dependence of zeta potential of various polymers on GCC slurry (0.02 wt.%)



2. Effect of polymer dosage level on first-pass fines retention (FPFR). Papermaking stock was flocculated with cationic linear polyacrylamide (C-PAM1). Addition levels of microparticles were twice as much as polymer levels—HwBKP: 1.75 g, GCC: 0.75 g, agitation speed: 750 rpm.

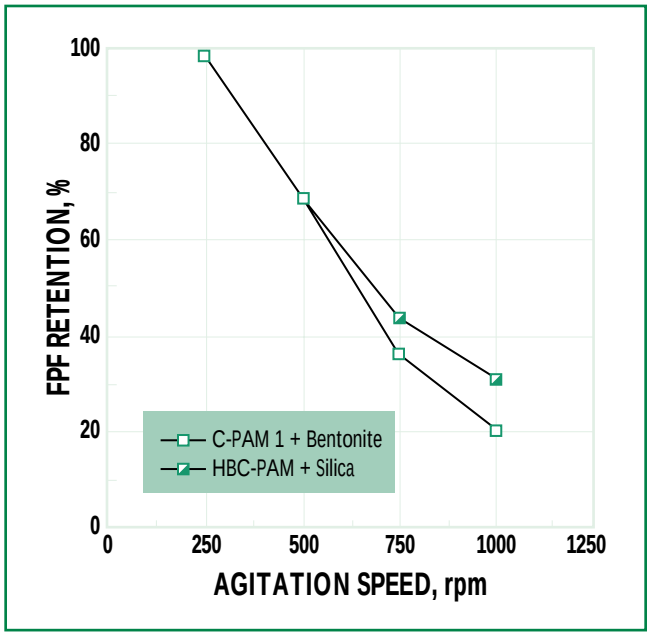


3. Effect of polymer dosage level on first-pass fines retention (FPFR). Papermaking stock was flocculated with highly branched cationic polyacrylamide (HBC-PAM). Addition levels of microparticles were twice as much as polymer levels—HwBKP: 1.75 g, GCC: 0.75 g, agitation speed: 750 rpm.

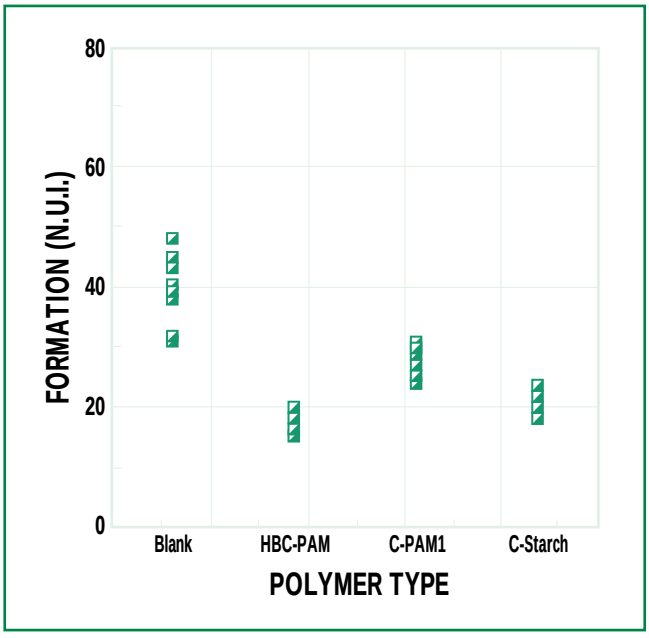


4. Plot of polymer type vs. first-pass fines retention (FPFR). Stocks containing fiber, fines, and GCC were flocculated with 0.1 wt.% of polymers and 0.2 wt.% of microparticles. N-PAM, C-PAM1, and C-PAM2 were incorporated in microparticle system with bentonite, and HBC-PAM and cationic starch were incorporated with colloidal silica.

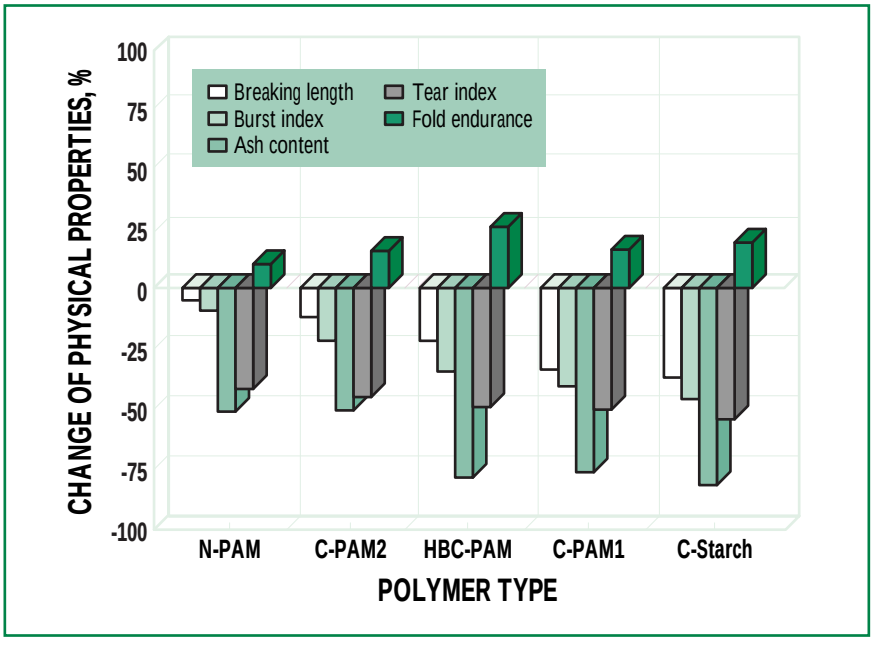
lower than 500 rpm, equivalent fines retention values are obtained for C-PAM1 and HBC-PAM. FPFR is decreased almost linearly as the agitation speed is increased to 750 rpm. However, the FPFR spread between the two systems becomes larger when the agitation speed is increased to 1000 rpm. This indicates that the tenacity of the flocs formed with HBC-PAM to high shear is greater than flocs formed with C-PAM1; this is completely coincident with the flocculation data of the previous paper.



5. Dependence of first-pass fines retention (FPFR) on agitation speed of dynamic drainage jar (DDJ). Polymer dosage level: 0.05 wt.%, microparticles: 0.1 wt.%.



7. Effect of polymer type on the formation of handsheets. HwBKP: 400 mL CSF, GCC: 30 wt.% on pulp, basis wt.: 60g/m², polymer dosage level: 0.1 wt.%, microparticles: 0.2 wt.%.



6. The change of ash contents and physical properties of handsheets on retention system. Papermaking conditions—HwBKP: 400 mL CSF, GCC: 30 wt.% on pulp, stock consistency: 0.7%, polymer dosage level: 0.1 wt.%, microparticles: 0.2 wt.%.

KEYWORDS
Acrylamide, acrylic compounds, amides, bentonite, branched chains, cationic compounds, fines, flocculation, polyacrylics, polyelectrolytes, polymers, retention aids, shear, synthetic silica.

Figure 6 shows the ash contents and mechanical properties of handsheets prepared using various retention systems. The handsheets were prepared from a masterbatch of a stock that contained 30 wt.% of GCC as a filler. Various polyelectrolytes and related microparticles were added to this papermaking stock. As shown in this figure, the highest ash retention is attained when HBC-PAM with colloidal silica is used as a retention aid. N-PAM gives the lowest ash retention value among the polyelectrolytes applied. Various mechanical properties were determined with the handsheets, and the percent reduction of strength properties was calculated according to the following equation:

$$C = [(S_u - S_f) / S_u] \times 100 \qquad (1)$$

where

C = change of physical properties, %
S_u = strength of unfilled sheet
S_f = strength of filled sheet.

The strength properties of handsheets generally decrease with an increase in filler retention. This is because the filler particles prevent hydrogen bonding between fibers; this is believed to be the most important factor in paper strength development. The decrement in strength property of the sheets formed with HBC-PAM is less than in those formed with C-PAM1

and cationic starch. Since the sheets formed with HBC-PAM as a retention aid contain more ash than the sheets formed with C-PAM1 and cationic starch, it is believed that the filler particles retained in the HBC-PAM sheets do not prevent interfiber bond formation as much as those contained in the sheets formed with C-PAM1 and cationic starch.

Figure 7 shows the effect of polymer type on the formation of the resultant handsheet. The handsheets formed with branched polymers, such as HBC-PAM and C-starch, have a better formation than the formation of a sheet with C-PAM1. The flocs formed by HBC-PAM, which are small and compact and have a high tenacity against high shear can be beneficial in achieving a paper with good formation. The results from Figs. 6 and 7 strongly indicate that the flocs distribute more evenly in the sheet when HBC-PAM with colloidal silica is used as a retention system.

CONCLUSIONS

Regarding the molecular shapes of polymers as retention aids, branched polymers show better retention efficiency than linear polyelectrolytes. Linear polymers used with plate-like bentonite show greater retention values. On the other hand, better retention of fines is achieved when spherical colloidal silica is used as a microparticulate retention additive with branched polymers. Since the flocs formed with HBC-PAM combined with colloidal silica are evenly distributed in the paper due to their small and compact structure, paper with good formation can be obtained. **TJ**

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LITERATURE CITED

1. Strazdins, E., *Tappi* 53(1): 80(1970).
2. Strazdins, E., *TAPPI 1988 Papermakers Conference Proceedings,* TAPPI PRESS, Atlanta, p. 379.
3. Horn, D. and Linhart, F., *Retention Aids in Paper Chemistry* (J. C. Roberts, Ed.), Chapman and Hall, New York, 1991, Chap. 4.
4. Moore, E. E., *Tappi* 59(6): 120(1976).
5. Britt, K. W. and Unbehend, J. E., *Tappi* 57(12): 81(1974).
6. Britt, K.W., *Tappi* 56(3): 83(1973).
7. Gill, R. I. S., *Paper Technology* 32(8): 34(1991).
8. Moberg, K., *TAPPI 1989 Retention and Drainage Short Course Notes,* TAPPI PRESS, Atlanta. 9. Shin, J.-H., Han, S. H., Sohn, C., *et al., TAPPI J.,* in press. p.65
10. Shin, J.-H., Han, S. H., Sohn, C., *et al., Proceedings of the 1993 (60th) Pulp and Paper Research Conference,* Japan TAPPI, Tokyo p. 86. 11. Britt, K. W., *Tappi* 59(2): 67(1976).
12. Unbehend, J. E., *Tappi* 60(7): 110(1977).
13. Brower, P. H., *Tappi J.* 74(1): 170(1991).