

Highly branched cationic polyelectrolytes: Filler flocculation

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PAPERMAKING TECHNOLOGY HAS been continuously advancing with the development of faster and more sophisticated paper machines and various chemical additives. Since the presence of high amounts of fines in the wet end influences retention, drainage, system closure, etc., promoting proper flocculation between fines and fibers for economic benefits and process improvements is desirable. In addition, the necessary flocculation must occur at high shear conditions accompanied by an increase in machine speed. Since mechanical means and process modifications have limits in achieving this goal, resorting to chemical means is necessary. Optimization of chemical formulation or additive use in papermaking has promoted flocculation for better retention.

Various polymeric flocculants such as polyacrylamides (PAM) (1-3), polyethylene imine (PEI) (4, 5), polyamines (6), polyamidoamines (7), polyethylene oxide (PEO) (8, 9), polydiallyldimethyl-ammonium chloride (p-DADMAC) (10), and modified starches (11) have found extensive use for this purpose during the last several decades. The careful control of papermaking chemistry with these electrically charged polymeric flocculants has resulted in many benefits. These include improved machine runnability, better paper qualities, more efficient use of raw materials, and effluent load reduction. Most colloidal particles in the papermaking system have negative charges. Because of this, cationic polyelectrolytes that adsorb readily onto anionic surfaces

by electrostatic interactions have been the primary choice of flocculants for papermaking. Some anionic, nonionic, or amphoteric polyelectrolytes have found use as retention aids.

Flocculants cause the fibers, fines, fillers and other colloidal particles to form an aggregate by either bridge or patch formation depending upon their molecular weight and charge density. A general belief is that polyelectrolytes with high molecular weight and low cationic charge density flocculate colloidal particles by bridging. Those with low molecular weight and high charge density form flocs by patch formation (12). Soft flocs formed by the patch formation mechanism are usually small and compact. Upon exposure to high turbulence, the soft flocs break easily. When the turbulence subsides, the same level of aggregation can recur. This shows the reversible nature of the flocs.

To a varying degree, hard flocs formed through a bridging of polyelectrolytes have a loose, voluminous structure. They show some resistance to high turbulence for a short period. They break irreversibly after subjection to longer periods of high turbulence. Both flocculation mechanisms are therefore insufficient to explain other phenomena in the papermaking process. For example, when hard flocs are produced for flocculation improvement, undesirable side effects such as poor paper formation and inferior sheet quality often result due to the voluminous structure of the flocs. Soft flocs show poor flocculation, since they readily disperse during turbulence.

FLOCCULATION

ABSTRACT

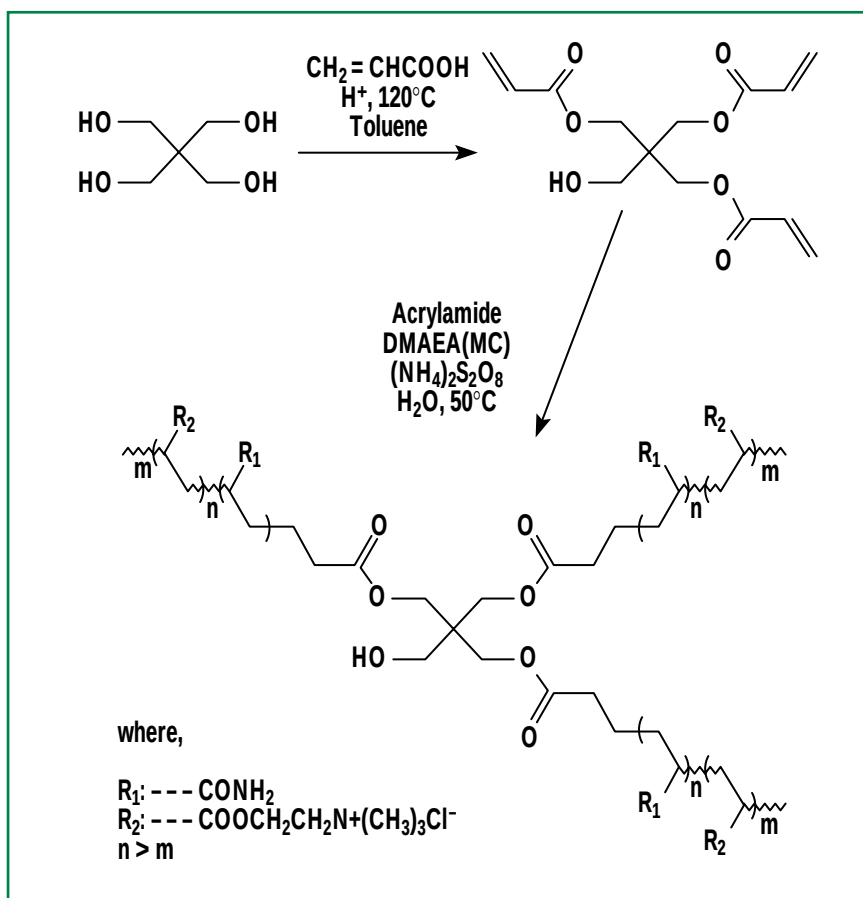
Highly branched cationic polyacrylamides of low molecular weight and low cationic charge density were investigated for flocculation of ground calcium carbonate and titanium dioxide particles. They were compared with conventional linear polyelectrolytes with special attention on the effect of polymer concentration and shear condition. Also examined was the microparticle addition effect on filler flocculation. The highly branched polymers produced small flocs with great shear resistance. Results show that adding microparticulate silica could further increase the floc size.

Application:

A highly branched cationic polyelectrolyte offers promise as a retention aid in a microparticulate retention system.

The ideal flocs from the papermakers' viewpoint are those that have compact structure, appropriate size, resistance to shear, and high retention properties. Since most flocculants currently used to generate flocs are either too large or too weak in tenacity against shear, there is a great need to develop a new flocculant and a method for its effective application.

Recently, Nicke et al. (13) have demonstrated a novel branched copolymer polymerized from diallyldimethyl-ammonium chloride (DADMAC) and approximately 1.5% by weight of triallylmethylammonium chloride as an attractive flocculant for the paper industry. In addition, recent calculations for dilute systems indicate that polymer tails determine the hydrodynamic thickness of the adsorbed layer almost exclusively (14). These studies suggest the importance of polymer configuration in flocculation. After investigating the mechanisms of flocculation of kaolin suspensions with cationic polyacrylamides of varying molecular weight but similar



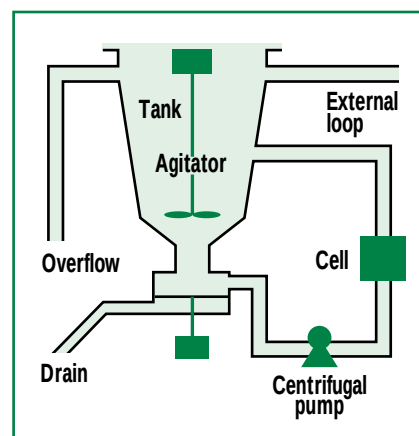
1. Synthetic route and designed molecular structure of HBC-PAM based on PETA, AM, and DMAEA-MC

EXPERIMENTAL

cationic charge, Gill and Herrington (15) have shown that at and below a molecular weight of one million, charge neutralization begins to take precedence to bridging as the mechanism of particle destabilization.

This encouraging information has prompted the development of a highly branched cationic flocculant of low molecular weight and low cationic charge density. Branches or tails on highly branched polymers may extend into the aqueous medium after adsorption. The bridging flocculation of colloidal particles using these stretched tails could occur despite low molecular weight. The purpose of our study was to synthesize such highly branched cationic polyelectrolytes based on acrylamide (HBC-PAM) and to examine their flocculation behavior.

HBC-PAMs were polymerized by ammonium persulfate as an initiator with pentaerythritol triacrylate (PETA), acrylamide (AM), and the methyl chloride salt of dimethylaminoethylacrylate (DMAEA-MC) as a cationic co-monomer. PETA, a trifunctional polymerizable compound, was synthesized for use as a branching material (16). Figure 1 shows the synthetic route (17) and designed molecular structure of HBC-PAM. The polymerized HBC-PAM was purified by precipitation in methanol—a nonsolvent for this polymer. The unreacted monomers and PETA were removed by methanol washing, and the HBC-PAM was precipitated. Cationic linear polyacrylamides (C-PAM) with different molecular weights were also polymerized for comparison. Two linear C-PAMs—one with a very high molecular weight (C-PAM 1) and the other



2. Schematic diagram of particle size analyzer

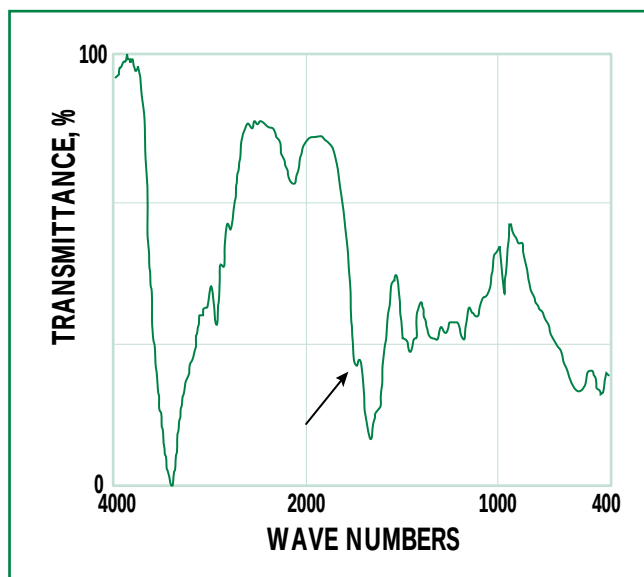
with a moderately high molecular weight (C-PAM 2)—were prepared. Both polymers had low cationic charge density.

To evaluate the flocculation behavior of polymers, slurries of ground calcium carbonate (GCC) and titanium dioxide were used. Change of the floc size of filler formed by polymeric flocculants was traced as a function of flocculation time and centrifugal pump speed. Floc size and size distribution were determined by particle size analyzer. The number-averaged floc size of filler was derived from the curves of floc size distribution. Number-averaged floc size was simply denoted by average floc size. The centrifugal pump in the size analyzer was designed to impart shear force to the filler flocs. As the pump speed increased, the shear force applied to the filler flocs increased. Figure 2 shows a schematic diagram of the instrument. Table I lists the materials for this experiment with their typical properties.

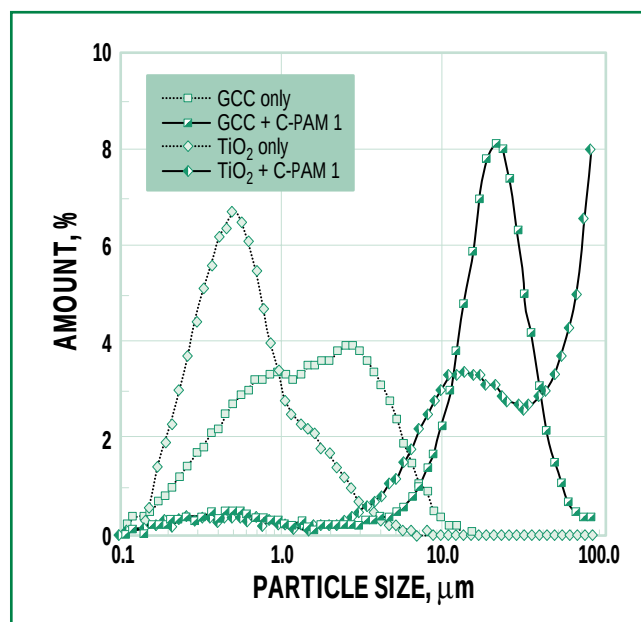
RESULTS AND DISCUSSION

Configuration of HBC-PAM

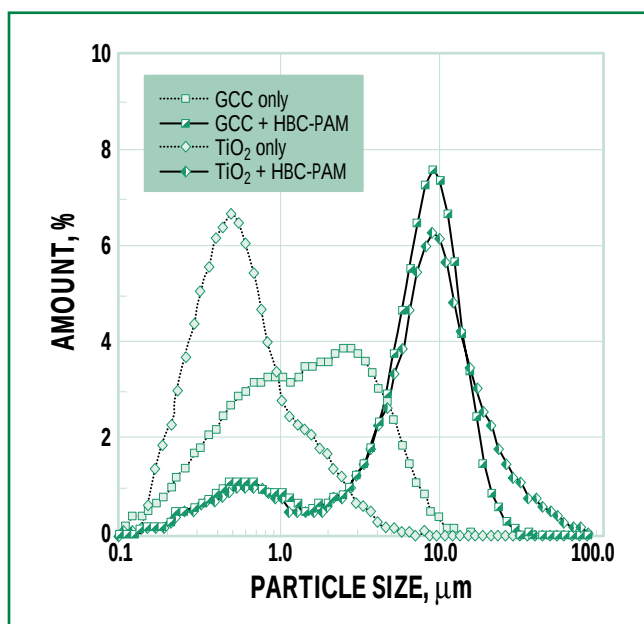
Figure 3 shows a FTIR spectrum of the purified HBC-PAM. The characteristic peak of a carbonyl group at 1735 cm⁻¹ due to the ester group of PETA remains unchanged by the methanol washing in the purification process. This peak implies that the PETA is in the polymer chain of the HBC-PAM. Crosslinking of the polymer chains is generally inevitable when the poly-



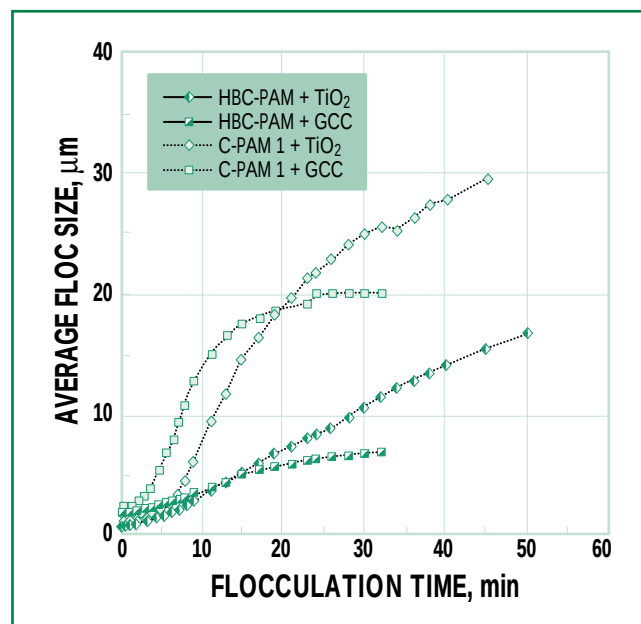
3. FTIR spectrum of HBC-PAM based on PETA, AM, and DMAEA-MC



4. Particle size distribution curves of GCC and titanium dioxide after flocculating with 0.05% by weight of C-PAM 1 for 30 min with 675-rpm agitation speed and 1350-rpm pump speed



5. Particle size distribution curves of GCC and titanium dioxide after flocculating with 0.05% by weight of HBC-PAM for 30 min with 675-rpm agitation speed and 1350-rpm pump speed



6. Dependence of average floc size on the flocculation time when treating GCC and titanium dioxide with HBC-PAM and C-PAM 1 with 0.05% by weight polymer dose, 675-rpm agitation speed, and 1350-rpm pump speed

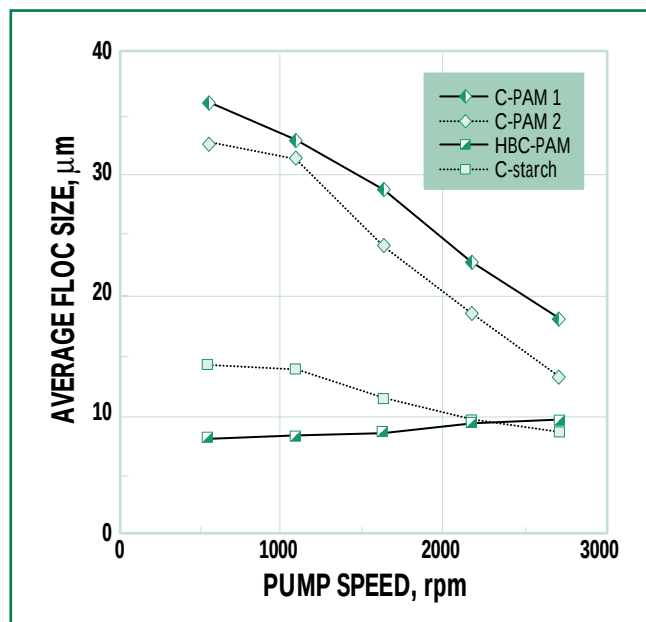
merization via a radical mechanism occurs in the presence of a polyfunctional compound. Most cross-linked polymers are not soluble in any solvents due to the formation of a three-dimensional network structure. The HBC-PAM polymerized in this study

was completely soluble in water meaning no insoluble network portion.

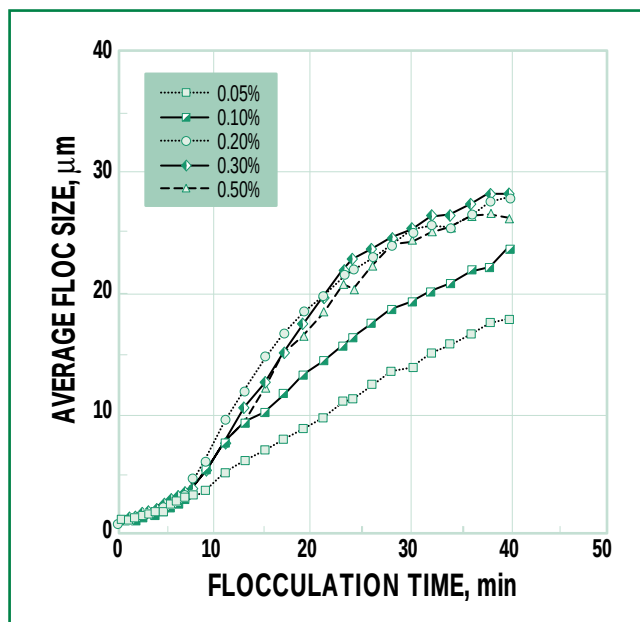
Flocculation behavior

Figures 4 and 5 show particle size distribution curves of the GCC and titanium dioxide used in this study with

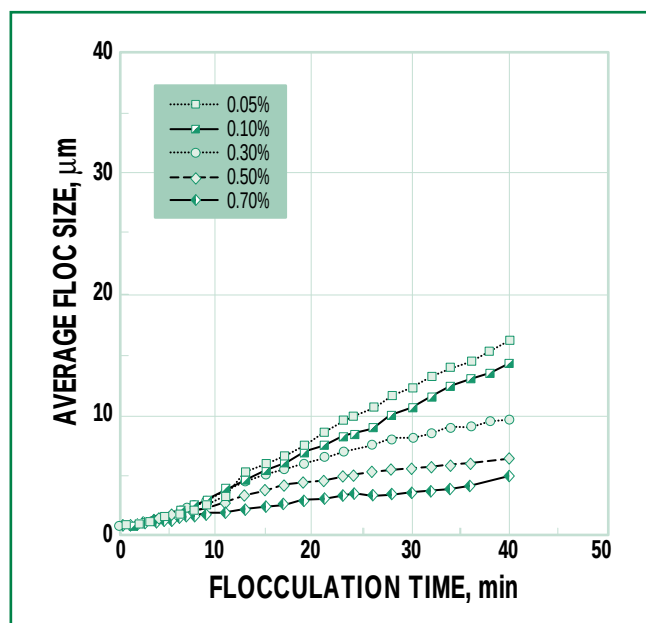
the floc size distribution curves after flocculating with 0.05% of C-PAM 1 and HBC-PAM, respectively. These figures show that unflocculated GCC shows greater average particle size and broader particle size distribution than titanium dioxide. The size distrib-



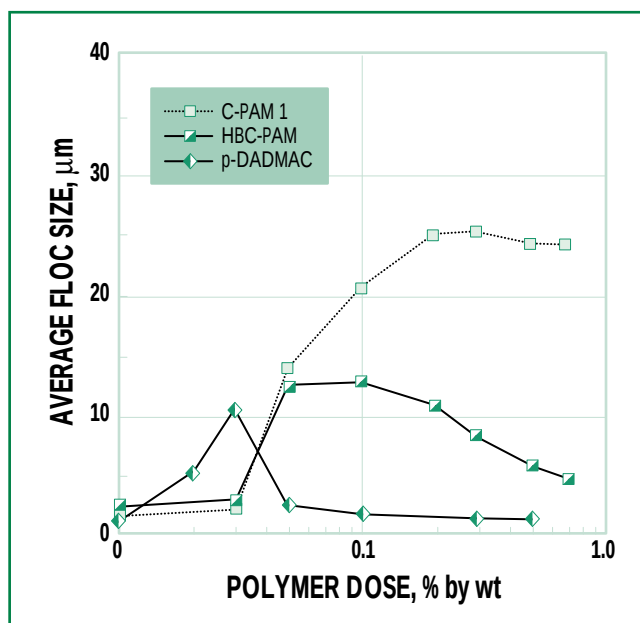
7. Dependence of average floc size of titanium dioxide on the centrifugal pump speed at constant agitation speed of 1350 rpm using polymer dose levels of 0.05% by weight except 1.0% by weight for C-starch



8. The average floc size of titanium dioxide as a function of flocculation time at various C-PAM 1 dose levels with 675-rpm agitation speed and 1350-rpm pump speed



9. The average floc size of titanium dioxide as a function of flocculation time at various HBC-PAM dose levels with 675-rpm agitation speed and 1350-rpm pump speed



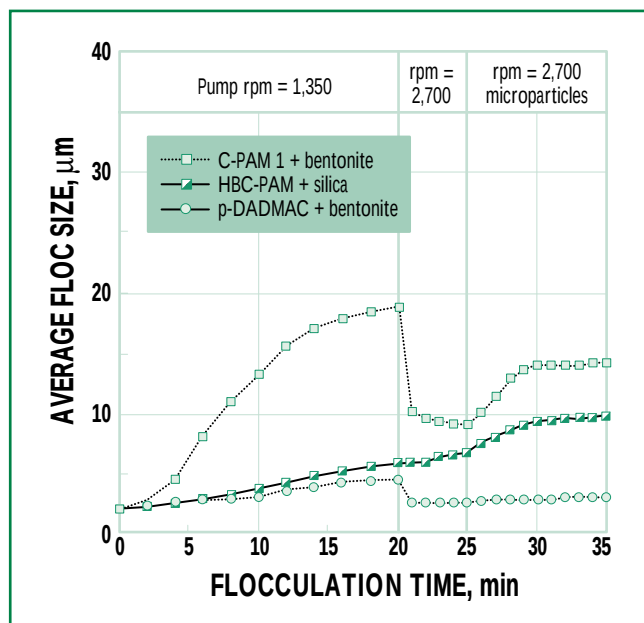
10. Plot of average floc size of titanium dioxide vs. polymer dose levels for 30-min flocculation time, 675-rpm agitation speed, and 1350-rpm pump speed

ution range and average size values reversed when flocculated with C-PAM 1 for 30 min. This shows greater average particle size and broader particle size distribution for titanium dioxide particles flocculated by C-PAM 1. When the same fillers are flocculated

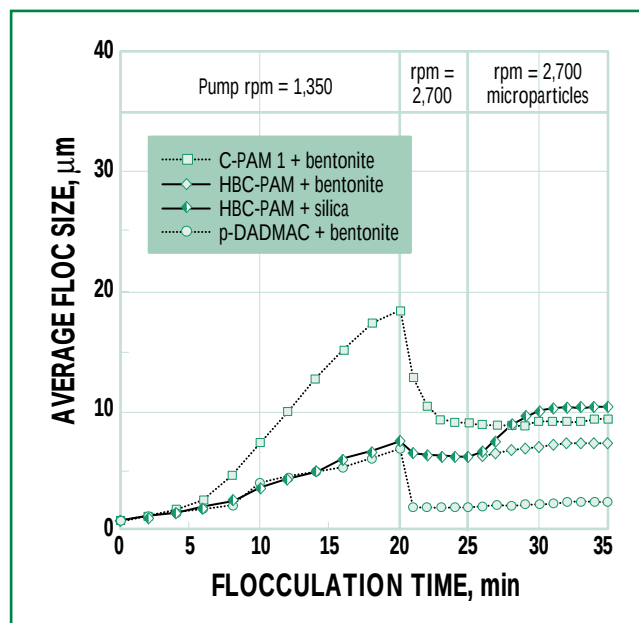
with HBC-PAM at the same conditions, flocs of smaller average size are obtained as Fig. 5 shows. The floc size distribution curves also have narrower widths suggesting that HBC-PAM forms more homogeneous flocs. These improvements should be beneficial for

paper formation and other physical properties.

Figure 6 shows that the average floc size of GCC and titanium dioxide slurries flocculated with C-PAM 1 and HBC-PAM depends on flocculation time. The flocculation time is the time



11. Effect of flocculation time and external shear on average floc size of GCC under various conditions with 0.05% by weight polymer dose level, 0.2% by weight of bentonite, and 0.1% by weight of silica



12. Effect of flocculation time and external shear on average floc size of titanium dioxide under various conditions with 0.05% by weight polymer dose level, 0.2% by weight of bentonite, and 0.1% by weight of silica

from the addition of flocculant into the filler slurry to the determination of floc size at the same conditions. The average floc size increases continuously with time indicating the involvement of kinetic aspects in the flocculation process. The average floc sizes of fillers are greater when C-PAM 1 is the flocculant.

Effect of shear force and polymer concentration

Since the formed flocs must survive during further shear in the paper machine or reform after points of high shear, producing tenacious flocs resistant to high shear is essential. The disruption of flocs by shear relates to size. Larger aggregates undergo easier disruption (18, 19). The filler retention achievable with high molecular weight polyelectrolytes decreases rapidly when the stirring speed of a dynamic drainage jar (DDJ) exceeds 1000 rpm (20). This indicates the limited strength of the flocs. Hard flocs formed with high molecular weight polyelectrolytes have irreversible reflocculation characteristics when exposed to strong shear. These characteristics of hard flocs limit the addition

of the polymer to a point after the machine parts producing strong shear such as cleaners and screens.

We investigated the effect of shear force on floc size formed with various polymeric flocculants by changing the pump speed of the particle size analyzer. Figure 7 compares C-PAM 1 and C-PAM 2 with a cationic starch (C-starch) and HBC-PAM. When increasing the shear force by increasing the pump speed, the average floc size decreases substantially for the linear C-PAMs. This indicates their limited tenacity against high shear. The average floc size when exposed to strong shear decreases slightly with the C-starch and remains unchanged with HBC-PAM. This finding indicates that the flocs formed by the branched polymer are smaller but more tenacious flocs than those formed by the linear polymers.

The concentration of polyelectrolyte strongly influences the average floc size flocculated by polymers. As Figure 8 shows, C-PAM 1, a cationic linear polyacrylamide with a high molecular weight and low cationic charge density, flocculates titanium dioxide particles extensively. The average floc size

increases significantly and then reaches an equilibrium condition with increasing polymer concentration. This is a typical flocculation behavior for this type of polymer signifying a bridging flocculation mechanism. The average floc size of titanium dioxide flocculated by HBC-PAM decreases as the polymer dose increases. This suggests a different type of flocculation mechanism as Figure 9 shows.

When using a cationic linear polyelectrolyte with high charge density and low molecular weight like p-DADMAC, flocculation occurs from attractive forces between oppositely charged patches of colliding particles. In such a case, the curve with maximum value occurs when plotting the average floc size as a function of polymer dose. When polyelectrolyte flocculates colloidal particles by a bridging mechanism, the average floc size increases continuously as the addition level increases. Figure 10 shows this type of flocculation for C-PAM 1. The flocculation pattern for HBC-PAM suggests that neither a charged patch nor a bridging mechanism apply for this polymer.

Materials	Molecular shape	Viscosity at 25°C, cPs	Charge density at pH 4.5, (meq/g)
C-PAM 1	Linear	1080	1.9
C-PAM 2	Linear	640	1.8
p-DADMAC	Linear	10	7.1
C-Starch	Branched	100	0.4
HBC-PAM	Highly branched	330	1.6
Colloidal silica	Spherical	-	-
Bentonite	Plate-like	-	-

(Polymer viscosities used a Brookfield viscometer (RV, No. 4 spindle) at 1.0 wt.% polymer solutions.)

I. Properties of materials used in the experiment

We have also examined shear resistance of the GCC flocs. For this investigation, the polymeric flocculants are added to the GCC slurry. The GCC flocs are then subjected to shear conditions of 1350 rpm for 20 min followed by raising suddenly to 2700 rpm. After 5 min at 2700 rpm, microparticles (bentonite or silica) commonly used in the papermaking industry as a retention additive are added to the system followed by an additional 10 min of high shear. The results plotted in **Fig. 11** show the effects of flocculation time and external shear on the average floc size of GCC under varying conditions. Small flocs are produced with p-DADMAC. Bulkier flocs form with C-PAM 1 at a pump speed of 1350 rpm. Noticeable changes occur when the pump speed increases from 1350 rpm to 2700 rpm for these flocs. As this figure shows, GCC flocs produced by adding 0.05% of p-DADMAC are disrupted by the increased shear to give an average floc size similar to that of the unflocculated GCC. The voluminous GCC flocs formed by C-PAM 1 are also deflocculated with the increase of the pump speed. The average size of the GCC flocs flocculated with HBC-PAM is maintained around 10 μm indicating

their tenacity against shear. The accepted definition of the fines fraction is that the particles pass through a 75- μm hole (200 mesh) (21). There are two general aspects of the retention of fine particles: mechanical entrapment and colloidal forces. The average floc size of 10 μm —the maximum size flocculated with HBC-PAM—seems too small to retain the filler particles in the finished paper. This floc system is therefore flocculated only by electrostatic colloidal forces. A separate paper will discuss retention results including mechanical entrapment in detail.

The results strongly indicate that p-DADMAC forms soft flocs and C-PAM 1 produces hard flocs. For HBC-PAM, the average floc size of GCC is similar to that with p-DADMAC at a low shear condition. These flocs show a great tenacity against high shear as **Fig. 11** shows. When adding the microparticles to the deflocculated slurries of GCC, a significant increase in floc size occurs with C-PAM 1 and HBC-PAM. This suggests that these two polymers can also act as flocculants for the microparticle retention system (22).

A similar experiment using titanium dioxide gave the same trend as **Fig. 12** shows. When adding the microparticles into the deflocculated slurries, no detectable change in average floc size occurs for C-PAM 1 and p-DADMAC. The floc formed with HBC-PAM increases in size by the microparticle addition especially when using colloidal silica.

HBC-PAM shows a flocculation behavior different from C-PAM 1 and p-DADMAC. HBC-PAM produces small flocs with great shear resistance. The average floc size also can increase further by silica addition. The filler particle sizes, molecular weights and types of flocculants, and microparticles apparently play significant roles in the microparticle retention system. Small floc size and great tenacity against shear characteristically differentiate the HBC-PAM flocs from those formed by conventional linear flocculants. These characteristics have significant application potentials for the microparticle retention system. HBC-PAM requires no strong shear to destroy the preformed flocs. This allows a greater degree of freedom in the selection of the addition point for this polymer.

CONCLUSIONS

When using HBC-PAM as a flocculant for GCC and titanium dioxide particles, smaller flocs with greater shear resistance are produced compared with the conventional linear polyelectrolytes of high molecular weights. Experimental results indicate that the flocs formed with HBC-PAM have a compact structure with filler particles interconnected by the flexible polymer tails. Results clearly show that flocculation by HBC-PAM does not follow either charged patch or bridging mechanism. The floc size can increase further by adding microparticulate silica. This suggests the potential applicability of HBC-PAM as a retention aid in the microparticulate retention system. **TJ**

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KEYWORDS

Acrylamide, branched chains, cationic compounds, cross linking, flocculation, polyacrylics, shear stress, synthetic polymers, tensile strength.

LITERATURE CITED

1. Bikals, N. M., in *Water-Soluble Polymers* (N. M. Bikals, Ed.), Plenum Press, New York, 1973, p. 213.
2. Swift, A. M., *Tappi* 40 (9):224A (1957).
3. Volk, H. and Freidrich, R. E., in *Handbook of Water-Soluble Gums And Resins* (R. L. Davidson, Ed.), McGraw-Hill, New York, 1980, Ch. 16.
4. Wilfinger, H. and Auhorn, W., *Wochenblatt fur Papierfabrikation* 96:201 (1968).
5. Wilfinger, H., *Das Papier* 2:265 (1948).
6. Suen, T. J., Senior, A., Swanson, D. L., et al., *J. Polymer Sci.* 45:289 (1960).
7. Espy, H. H. and Putnam, S. T., U.S. pat. 3,951,921 (1976).
8. Leung, P. S. and Goddard, E. D., *Tappi J.* 70(6):115 (1987).
9. Manley, J. A., U.S. pat. 3,141,815 (1964).
10. Butler, G., in *Polymeric Amines And Ammonium Salts* (E. J. Goethals, Ed.), Pergamon Press, Oxford, 1980, p. 125.
11. Rutenberg, M. V., in *Handbook of Water-Soluble Gums And Resins* (R. L. Davidson, Ed.), McGraw-Hill, New York, 1980, Ch. 22.
12. Unbehend, J. E., *Tappi* 59(10):74 (1976).
13. Nicke, R., Pensold, S., Tappe, M., et al., *Wochenblatt fur Papierfabrikation* 120(14):559 (1992).
14. Scheuthens, J. J. H. M., Fleer, G. J., and Cohen Stuart, M. A., *Colloids and Surfaces* 21:285 (1986).
15. Gill, R. I. S. and Herrington, T. M., *Colloids and Surfaces* 25:297 (1987).
16. Shin, J. -H., Han, S. H., Ow, S. K., et al., *J. Kor. Fiber Soc.* 31:89 (1994).
17. Shin, J. -H., Han, S. H., and Ow, S. K., *Coop. Treaty pat. WO 95/03450* (1995).
18. Hubbe, M. A., *Colloids and Surfaces* 16:249 (1985).
19. Pandya, J. D. and Spielman, L. A., *J. Coll. Interface Sci.* 90(2):517 (1982).
20. Britt, K. W., *Tappi* 56(10):46 (1973).
21. Unbehend, J. E. and Britt, K. W., in *Pulp and Paper— Chemistry and Chemical Technology* (J. P. Casey, Ed.), 3rd edn., Vol. III, Wiley, New York, 1981, p. 1954.
22. Gill, R. I. S., 1991 PIRA Conference Proceedings, PIRA, Surrey, paper 02.

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