Flocculation Characteristics of Copolymer of Acrylamide with Quaternary Ammonium Cationic Monomer (Running) Flocculation by Cationic polyacrylamide

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Abstract: Copolymers of acrylamide (AM) and acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC) synthesized by dispersion polymerization in aqueous media were evaluated as flocculents and retention aids in papermaking. The flocculation of a model CaCO₃ suspension was monitored by measuring the floc size using a particle size analyzer. The effects of the molecular weight, copolymer, and shear on flocculation were investigated. The cationic copolymers exhibited an improved flocculation behavior compared to the homopolymer, polyacrylamide, plus the floc size increased with an increase in the molecular weight. The copolymers showed also a better shear resistance than the homopolymer. The flocculation was more sensitive to the molecular weight of the copolymers than to the copolymer composition or charge density of the copolymers. It was also shown that the copolymers prepared in a dispersed state could be applied as efficient retention aids in papermaking.

Keywords: acrylamide (AM), acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC), dispersion polymerization, flocculation, retention aid

Introduction

Paper is produced by draining paper furnish on a paper machine wire. To control the quality of paper, fillers and chemicals are added to the pulp. However, in actual practice, the rush of water through the wire carries away a large portion of the fines (fine fibers) and fillers. As such, avoiding the loss of fines in the effluent water (white water) and the recovery and re-circulation of the white water constitute a major challenge for the paper industry. The higher the proportion of fines retained by the paper sheet, the more efficient the entire operation [1-5]. In order to link fines effectively into a coherent sheet, retention aids are routinely used [6,7]. Although various retention systems are used, the net effect is the same: the fines and fillers need to be effectively retained in the fiber mat during sheet formation. The basic mechanism is charge neutralization when a cationic polymer is added to ionic slurry of pulp. The fines and fillers coagulate because the polymer reduces the charges of the electrical double layer, and as the layer is neutralized the flocculation then occurs.

Currently, there is a growing interest in the use of acrylamide-based cationic polyelectrolytes as retention aids and flocculents. Cationic polyelectrolytes can be prepared by modifying polyacrylamide (PAM) or by copolymerizing acrylamide (AM) with comonomers including cationic charged groups [8-13]. During the last 30 years, the manufacture of AM homo- and copolymers has rapidly increased, partly due to their many applications (e.g., papermaking, waste treatment, and mineral processing) [14-19] and partly due to the important technical advances made in the controlled homo- and copolymerization of acrylamide [20-25]. PAM can also be modified by Mannich and Hoffman reactions to provide cationic flocculants with relatively high molecular weights [26-29].

A new experimental copolymer was recently developed by the current authors and would appear to be promising...
as a retention aid. The copolymer structure, shown in Figure 1, consists of a long poly(acrylamide -co-acryloyloxyethyl dimethylbenzyl ammonium chloride) (AODBAC) (molecular weight >10^6). Previous laboratory work showed that the copolymer could be prepared by radical initiated dispersion polymerization in an aqueous solution of ammonium sulfate using the poly(acryloyloxyethyl trimethyl ammonium chloride) (PAOTAC) as the stabilizer [30]. Conventionally, PAM and copolymers with AM are prepared by emulsion, precipitation, and solution polymerization. However, these polymers in dry form are difficult to dissolve. Moreover, their solutions are also difficult to handle because they either give rise to a gel or become too diluted for the application. Various methods have been proposed to overcome these problems related to solution application; one uses inverse emulsion and inverse microemulsion (water in oil) [31-33], while another uses finely divided polymer dispersions in water or mixtures of alcohol and water [34-37]. In the latter case, if a polymer can be finely dispersed by dispersion polymerization in an aqueous medium with no organic solvent, it can be directly applied as prepared, especially to flocculation and papermaking. Furthermore, when compared with precipitation and solution polymerization, the solid products do not require separation and drying or the products re-dissolution for application.

Although several reviews about polymer flocculation have already been published [38-42], little is known about the floc size and process of flocculation. One of the reasons may be that indirect methods (e.g., turbidity, sedimentation rate) are usually applied to monitor flocculation. As such, only certain overall parameters are measured and no information is ascertained about the aggregate size as a function of time. Accordingly, this paper presents some new information on the floc size relative to the turbidity during the flocculation of calcium carbonate obtained using a particle size analyzer. This instrument can be used to determine the aggregate size of a flocculating system very accurately.

As such, the objective of this study was to evaluate copolymers as floculants for calcium carbonate (CaCO₃) used as a filler and retention aid in papermaking (a pulp and paper stock). The tasks included the investigation of the effects of the molecular weight, charge density, and polymer dosage on the floc size and establishing the optimum conditions for floc formation.

**Experimental Section**

**Materials**

Hardwood bleached kraft pulp (Hw-BKP) was purchased from Shinmooring Paper MFG. Co. Ltd. Ground calcium carbonate (GCC) was purchased from Omya-Korea Co. Ltd. The volume-average diameter of the GCC particles was 4.0 ± 0.23 μm from a particle size analyzer, Mastersizer x (Malvern, UK). Polyacrylamide and a copolymer of acrylamide-co-acryloyloxyethyl dimethylbenzylammonium chloride (AM-AODBAC) were synthesized by dispersion polymerization in aqueous ammonium sulfate media with poly (acryloyloxyethyl trimethylammonium chloride) (PAOTAC) as the polymeric stabilizer and 2,2'-azobisis(2-methyl propionamidine) dihydrochloride (AlBA) as the initiator. The detailed synthetic procedures are described in a previous paper [30]. The charge densities of the copolymers were measured by a particle charge detector, PCD 02 of MÜNTEK [30]. The molecular weights were measured by GPC, VISCOTEK model 250 with TOSOH G6000 PWxL and G5000PWxL columns using 0.3 mol/L acetic acid and 0.3 mol/L sodium acetate aqueous solution as a mobile phase at 30°C. DR-2505, a commercial product in a dispersed state with about 20 wt% of solid contents from Nalco Co., was used for comparison. The DR-2505 contained a copolymer of acrylamide plus a cationic comonomer and other constituents that were not generally known. To eliminate the effects of the other unknown constituents, DR-2505 was diluted in water, separated by dialysis using a porous cellulose acetate membrane [43] and then dried by lyophilization. The molecular weight was determined to be 8.0 × 10⁶ from an analysis by GPC measurement.

**Floc Size Measurement for CaCO₃**

The changes in the particle size of the filler (calcium carbonate) flocs after the addition of the polymeric retention aids were traced as a function of the flocculation time and centrifugal pump speed. As with DR-2505, the synthesized polymer used in this measurement was separated by dialysis using a porous cellulose acetate membrane and then dried by lyophilization. The particle size and size distribution were analyzed using a Mastersizer x (Malvern, UK). The centrifugal pump in

![Figure 1. Chemical structure of copolymer of acrylamide (AM) and acryloyloxyethyl dimethylbenzyl ammonium chloride (AODBAC).](image-url)
the Mastersizer \( \chi \) was designed to impart shear force to the filler flocs. The basic principle of the Mastersizer \( \chi \) is simple. The beam from a low power visible wavelength laser is first expanded and spatially filtered to provide a clean, parallel beam about 18 mm in diameter. As the beam passes through the particles, they scatter or diffract the light at different angles depending upon their diameter; large particles scatter at small angles and vice versa. The signals from the detector are then analyzed by the computer to provide the particles size distribution.

A stock suspension was prepared by dispersing 10 g of CaCO\(_3\) powder in 90 g of deionized water. After mixing overnight, the suspension was placed in an ultrasonic bath for 3 h.

A 3 mL volume of the CaCO\(_3\) suspension was added to 600 mL of water, then after the addition of 0.3 mL of the 0.05% polymeric flocculent solution the floc size of the CaCO\(_3\) suspension was continuously monitored by Mastersizer \( \chi \).

**Turbidity Measurement for White Water**

A furnish containing 2.25 g of hardwood bleached kraft pulp (Hw-BKP) refined to 350 mL Canadian Standard Freeness (CSF) and 0.96 g of ground calcium carbonate (GCC) as the filler was placed into the retention drainage analyzer (RDA) and water was added under stirring to make a total volume of 750 mL of the paper stock. Based on this measurement, the synthesized polymer dispersions were then used as prepared. The dispersions contained 5.5~10 wt\% of the copolymers and also contained 25 wt\% of ammonium sulfate and 0.5 wt\% of the stabilizer in water. The average diameters of the copolymer particles ranged from 3.6 to 6.7 \( \mu \)m. The amount of polymer added was 0.1~0.5 wt\% of fibre. The polymer dispersion was added to the RDA, and then the stock was stirred at 800 rpm for 2 min and drained on a 150 mesh screen. The drained effluent was analyzed based on the turbidity measurement using a Hach DR/2010 turbid meter. The measuring cell of the turbid meter was 25 mL, plus it was equipped with a high-intensity light emitting diode (wavelength 820 nm) and photodiode to detect the transmitted light. A sample without the added polymer was used as the blank. The relative turbidity was calculated using:

\[
T_r = \frac{T}{T_o}
\]

where \( T \) is the turbidity of the treated samples, and \( T_o \) is the turbidity of the blank.

**Results and Discussion**

**Comparison of Homopolymer with Copolymer for Flocculation of CaCO\(_3\)**

The particle size changes of GCC during flocculation with a 0.05% solution of polyacrylamide (PAM) and cationic polyacrylamide (PAODBAC-AM) are compared in Figure 2. The average floc sizes and relative turbidity of GCC exhibited a certain relationship, as shown in Figure 2. The average floc sizes of GCC increased with time after the addition of the polymers, due to the adsorption of the polymer inducing aggregation. When the polymer–particle adsorption reached equilibrium, the particle size leveled off.

PAODBAC-AM exhibited a better flocculating performance than homo-PAM because its cationic groups were able to reduce the surface potential of the particles, thereby facilitating the floc formation. The PAODBAC-AM, with opposite to those on the particle surface, continued to adsorb strongly until the particle charge was neutralized, and hence assisted the flocculation by reducing the electrical repulsion of the electrical double layer. In contrast, with a nonionic polymer such as PAM, the adsorption most likely occurred through hydrogen bonding, which is weaker than the electrostatic attraction, plus the polymer backbone will function as a bridge to link the particles. The oxide particles have a surface layer of hydroxyl groups and these groups were available for hydrogen bonding with the amide group in PAM [44].

**Effects of Polymer Molecular Weight on Flocculation of CaCO\(_3\)**

The effect of the polymer molecular weight (MW) of the PAODBAC-AM on flocculation is presented in Figure 3. The molecular weights and the charge densities

![Figure 2. Comparison of average floc size during flocculation of CaCO\(_3\) suspension by PAM and PAODBAC-AM: ●, ○: 0.3 mL of 0.05 wt% PAM (Mw=5.58 \( \times \) 10\(^6\)), ■, □: 0.3 mL of 0.05 wt% PAODBAC-AM (Mw=6.08 \( \times \) 10\(^6\), Expt. no. 4); stirrer speed= 675 rpm.](image-url)
of the copolymers are presented in Table 1. The average floc sizes for PAODBAC-AM showed a strong dependence on the polymer molecular weight. The higher the MW is the larger the floc size becomes. The floc size for a copolymer with a molecular weight of 3 million was 24.65 μm. When the molecular weight of the copolymer was doubled, the floc size increased to 30.45 μm. Similar results have also been previously reported [45-48]. The usually explanation is that the longer chains are more effective in bridging more particles.

**Effects of Copolymer Composition on Flocculation of CaCO₃**

The average floc size was influenced by both the composition of AODBAC and the charge density of the cationic copolymer. The curves in Figure 4 show the results from four series of copolymers with different mole-ratios of AODBAC to AM. The charge densities and the molecular weights are presented in Table 2. As the AODBAC/AM ratio increased, the charge density increased. However the molecular weight did not change significantly. The PAODBAC-AM with a higher AODBAC ratio flocculated the GCC particles more slowly initially, yet after 30 min the floc size became larger with a higher AODBAC ratio. However, the difference in the final floc size (from 24 to 26 μm) was small.

For effective flocculation, the adsorption and bridging should be properly balanced. Polymer chains with too few charges would not provide enough adsorption while leaving longer bridging segments, whereas too many charges would make the adsorbed polymer chains flat on the surface while leaving shorter bridging segments. In addition, the cationic centers located on the bridging segments of the chains are not used for neutralization or

**Figure 3.** Effect of molecular weight on flocculation of CaCO₃: 0.3 mL of 0.05 wt% copolymer (in Table 1), DR=commercial products; stirrer speed = 675 rpm.

**Figure 4.** Effect of AODBAC/AM-composition in copolymer on flocculation; 0.3 mL of 0.05 wt% copolymer (in Table 2); stirrer speed = 675 rpm.

**Table 2.** Effect of the Composition of AM and AODBAC on the Charge Density.

<table>
<thead>
<tr>
<th>AODBAC/AM (mole ratio)</th>
<th>Charge density of AODBAC (meq/g) a</th>
<th>Mw (×10⁶)</th>
<th>Mn (×10⁴)</th>
<th>AODBAC composition in copolymer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>05 : 95</td>
<td>328</td>
<td>3.83</td>
<td>1.76</td>
<td>3.25</td>
</tr>
<tr>
<td>10 : 90</td>
<td>768</td>
<td>3.67</td>
<td>2.03</td>
<td>8.36</td>
</tr>
<tr>
<td>15 : 85</td>
<td>1123</td>
<td>3.29</td>
<td>2.44</td>
<td>14.7</td>
</tr>
<tr>
<td>20 : 80</td>
<td>1414</td>
<td>2.72</td>
<td>2.10</td>
<td>21.6</td>
</tr>
</tbody>
</table>

The monomer, salt, stabilizer, and initiator concentrations were kept constant at 5.5%, 25%, 0.5%, and 1.84 × 10⁻⁵ mol/L, respectively. a: total charge density--charge density of the stabilizer.

**Table 1.** Results of Copolymerization of Acrylamide and AODBAC in Ammonium Sulfate Solution Using AIBA as the Initiator in the Presence of PAOTAC as the Stabilizer at 45°C.

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>AODBAC+ AM a (%) w/v</th>
<th>AS (%) w/v</th>
<th>PAOTAC (%) w/v</th>
<th>AIBA (×10⁴ mol/L)</th>
<th>C.D. of AODBAC (meq/g) b</th>
<th>Mw (×10⁶)</th>
<th>Mn (×10⁴)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6</td>
<td>25</td>
<td>0.5</td>
<td>4.60</td>
<td>736</td>
<td>3.65</td>
<td>1.24</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>25</td>
<td>0.5</td>
<td>4.60</td>
<td>770</td>
<td>4.03</td>
<td>2.15</td>
</tr>
<tr>
<td>3</td>
<td>6</td>
<td>25</td>
<td>0.5</td>
<td>1.84</td>
<td>763</td>
<td>5.05</td>
<td>2.47</td>
</tr>
<tr>
<td>4</td>
<td>6</td>
<td>25</td>
<td>0.5</td>
<td>1.84</td>
<td>702</td>
<td>6.08</td>
<td>2.06</td>
</tr>
</tbody>
</table>

a: Molar ratio of AODBAC/AM = 1:9
b: C.D.: charge density of AODBAC in the copolymer = (total charge density) – (charge density of the stabilizer)
adsorption. Thus, the charge density has a counter-balancing effect between the adsorption and the bridging, which are the two key functions of polymers in flocculation. This may explain why the effect of the charge density was not significant on the flocculation. Accordingly, the flocculation appeared to be more sensitive to the molecular weight of the copolymers than to the contents of AODBAC.

Effects of Stirring on Flocculation of CaCO₃

Regarding the sheet formation on a paper machine, there is another condition that deserves special emphasis. First, sheet formation takes place under conditions of both turbulence and high rates of hydraulic shear. The fine retention is greatly influenced by the degree of turbulence or hydraulic shear during the sheet formation [1,49-52]. As such, the effect of shear on flocculation was investigated by changing the stirrer speed of the Mastersizer (Figure 5). When the stirrer speed was increased, the flocc size decreased significantly against a high shear. The flocc size changed from 32.52 μm at 270 rpm to 21.73 μm at 1350 rpm.

Figure 5 shows another comparison of the effects of the stirrer speed and polymer type on the flocc size. Although both the cationic copolymer and the homopolymer exhibited lower flocc sizes at higher stirrer speeds, the cationic copolymer seemed to be less sensitive to the hydrodynamic forces than the homopolymer. This may have been due to the stronger adsorption by the cationic copolymer compared with the homopolymer.

Effects of Polymer Molecular Weights on Retention for Papermaking

This section presents the turbidity measurements to explain how many fines in the furnish were retained in the sheet. A better retention produces a lower turbidity in the drained water.

Figure 6 shows the influence of the copolymer concentration and molecular weight on the retention in bleached hard wood pulp with a constant calcium carbonate content. The copolymer contained an AODBAC: AM mole ratio of 10:90 and had molecular weights of 4 to 6 million. As expected, the fine retention increased with the copolymer concentration and molecular weight. Generally, a high molecular weight results in a higher retention. Xiao and coworkers [45,46] and Lindstrom and coworkers [53,54] reported a similar result from copolymers with different the molecular weights ranging from 0.7 million to 5 million.

When compared with the commercial product with a higher molecular weight, the retention obtained by the copolymer with a molecular weight of 6 million was similar or better. It should be noted that the copolymers employed as retention aids were prepared as dispersions, containing a 5.5 to 10 wt% of the copolymer content and some salt. It is also noteworthy that the synthesized copolymer dispersions were directly applied and functioned well as a retention aid in papermaking.

Conclusions

A study was carried out on flocculation by a homopolymer of acrylamide and cationic copolymers with AODBAC synthesized by dispersion polymerization in an aqueous media. By using a particle size analyzer, it was clearly observed that the aggregate size changed relative to time. The effects of the molecular weight, copolymer composition, and shear on flocculation were examined, and it was found that a copolymer of AODBAC-AM exhibited a better flocculating performance than the homopolymers. The copolymers also
showed a better shear resistance. This was mainly due to the cationic centers in the copolymer chains which had opposite charges to those on the fibres and fillers, thereby resulting in a stronger adsorption. The flocculation by the copolymer is not significantly affected by the charge density, while it was strongly affected by the molecular weight. The retention in papermaking also increased with an increase in the molecular weight of the copolymers, while a synthesized copolymer dispersion produced a similar retention to a commercial product with a higher molecular weight. It is suggested that high molecular weight copolymers produce better flocculation through a bridging mechanism whereby long protruding tails extending from one particle were caught by another particle.

References

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