A Dynamic Study of the Effect of Cationic Starch Molecular Weight and Charge on Filler and Fines Flocculation, Deflocculation, and Reflocculation

Bob Shian-Hou Ching

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A DYNAMIC STUDY OF THE EFFECT OF CATIONIC STARCH MOLECULAR WEIGHT
AND CHARGE ON FILLER AND FINES FLOCCULATION, DEFLOCCULATION,
AND REFLOCCULATION

by

Bob Shian-Hou Ching

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A DYNAMIC STUDY OF THE EFFECT OF CATIONIC STARCH MOLEULAR WEIGHT AND CHARGE ON FILLER AND FINES FLOCCULATION, DEFLOCCULATION AND REFLOCCULATION

Bob Shian-Hou Ching, M.S.
Western Michigan University, 1986

A modified laboratory instrument was used to dynamically monitor the flocculation of fines and filler under various shear conditions on the "seconds" basis. A three-way factorial design and ANOVA were used to evaluate the significance of cationic starch molecular weight and charge in affecting fines and filler flocculation, deflocculation, and reflocculation. The reduction of molecular weight under high shear was suggested by the results. Both main effects and interaction effects of charge and molecular weight were important in determining flocculation. Charge was the only significant factor for the reflocculation process. Molecular weight was more important than charge in imparting shear resistance to the flocs. The linear behavior of the deflocculation curves was found to be associated with starches which promoted high shear-resistant flocs. Compression and shielding effects were used to interpret the phenomena. Molecular weight and charge were significant for the initial rate of deflocculation under 1100 rpm. The amount of flocculation and the amount of flocs retained in the deflocculation process were found to be the most important factors to determine polymer utility in the wet end.
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Bob Shian-Hou Ching
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CHAPTER I
INTRODUCTION

Polymeric flocculants are now extensively employed in many industrial areas such as water clarification, sewage treatment, industrial ore recovery, and paper manufacturing. The application of those flocculants for filler and fines retention has been extensively studied and well accepted in the paper industry. It is well-known that failure to control retention has numerous detrimental effects including poor saveall efficiency, high headbox consistency, loss of valuable material, low stock drainage and poor sheet quality.

In the paper manufacturing process, strong hydraulic shearing forces exist at many positions of the paper machine which serve to mix, pump, and distribute the stock. Previous studies have shown that flocs produced by polymers will be degraded when they are subjected to high shear and these flocs will reform if the shearing is reduced or stopped. The documentation of these phenomena is abundant, however, the dynamics of the system (flocculation, deflocculation, and reflocculation) have not been thoroughly investigated.

Although there is controversy among scientists about the exact mechanism of aggregation and retention of negatively charged particles by polymers of different charge levels and molecular weight, most agree that the following mechanisms are
involved: (a) charge neutralization by inorganic electrolytes and low molecular weight high-charge density polymers, (b) bridging by high molecular weight polymers, and (c) electrostatic patch formation by polymers with high charge densities.

A study including different molecular weight and charge densities of polymers in a variable shear field should yield a better understanding of how different flocculants perform during the flocculation, deflocculation, and reflocculation processes. Such knowledge should be useful in the optimization of papermachine systems for retention of pigments and fines.
CHAPTER II

LITERATURE REVIEW

Electrical Double Layer

The concept of double layer surface electrical charge of solids in contact with water is shown in Fig 1. Basically all materials become electrically charged when placed in water. The development of the surface charge is by three mechanisms: (1)

(1) Direct ionization
(2) Crystal lattice substitution
(3) Preferential adsorption of ions

The resulting charges on the surface of the material comprise a surface potential. This will attract a layer of counterions bound to the surface. This layer is referred to as the Stern layer. (2)

It is difficult to measure the magnitude of the charge at the surface. However, the potential at the shear plane between the adsorbed layer and the bulk solution can be measured. This potential is zeta potential. (3) Its value is equal to or slightly less than the potential at the Stern layer, depending on the location of the shear plane.

The diffuse layer is beyond this plane, where ionic composition gradually approaches that of the bulk solution. In this layer, counter ions will exist in greater numbers so that an
Figure 1. Electrokinetic Double Layer
overall charge balance exists as required by the electroneutrality of the solution. The charge level decreases exponentially with distance from the solid surface. The thickness of the electrical double layer depends on the concentration and valence of the counterions and the dielectric constant of the liquid. The Stern and diffuse layers represent the "double layer" phenomena.

DLVO theory

The interaction energies between charged particles in aqueous solution are described by the Derjaguin-Landau, Verwey-Overbeek (DLVO) theory of colloid stability. The basic concept of the DLVO theory is that the total interaction energy \( V_I \) between two colloidal particles is equal to the sum of the energy of repulsion \( V_r \) and the attractive energy \( V_a \):

\[
V_I = V_r + V_a
\]

The source of the repulsive potential energy is the interaction of the diffuse layers. Van der Waals' forces provide an attraction of each particle. If all of the colloid particles in a suspension are repelled from each other due to a large repulsive potential energy, the system is stable. If the particles are able to approach each other with sufficient kinetic energy to exceed the repulsive energy barrier, then the attractive forces cause the particles to flocculate.

Figure 2 shows the dependence of the repulsion \( V_r \) and
attraction(Va) potentials as a function of distance between charged particles. It also shows the total energy of interaction (Va + Vr) for three cases:

(1) Curve I represents a stable system
(2) Curve II represents a slowly coagulating system
(3) Curve III represents a rapidly coagulating or unstable system

Generally, flocculation can be achieved by addition of ions which will specifically adsorb to reduce the surface potential of the particles to a value low enough so that van der Waals forces can become effective.

Figure 2 Net Potential Energy of Interaction Between Particles

The addition of electrolytes causes a compression of the diffuse layer and a subsequent shift of counterions from the
diffuse layer to the Stern layer. This increased concentration of ions in the Stern layer reduces the Stern potential, and thus the height of the energy barrier. The attractive forces between particles may then operate to aggregate the system.

Steric Stabilization

Heller and Pugh (61) found that gold sols in aqueous dispersions are stabilized by addition of nonionic polymer and the stabilization effect of polymer increases with its molecular weight and concentration. They explained this stabilization by constructing a new model. The total interaction energy may be written in the form

\[ V = V_s + V_t + V_r \]

where \( V_s \) is the steric repulsive energy.

A number of equations for calculating the steric repulsive energy associated with dispersion stability have been derived theoretically from various points of view: e.g., from the thermodynamics of polymer solutions, from statistical thermodynamics and from mechanical analysis. (62) However, there is a certain difficulty in applying these theoretical equations to practical systems, because they involve many parameters which are experimentally unmeasurable such as the number of attached segments and the segment density distribution in the adsorbed layers.
Adsorption at Solid - Liquid Interfaces

The adsorption of polymers at solid-liquid interfaces is influenced by a number of factors: the molecular weight and structure of a polymer, the environment of the liquid phase, the charge of polymer, and the surface nature of the adsorbate and polymer.

Coco (27) explained the adsorption process for a wet end additive to function as follow:

(a) Transport from the bulk of the solution onto the interface of the solution and fiber.
(b) Material transport across the interface.
(c) Migration of the polymer into the material.
(d) Rearrangement of the polymer on the surface.
(e) Development of final bonding forces.

For high molecular weight polymers C is not significant, and the rate determining steps are probably B and D. For low molecular weight polymers C is significant. He also showed the role of molecular structures in developing the bonding forces. For a rigid rod-like polymer (guar), all the hydroxyl groups are exposed and available for hydrogen bonding. By contrast, in a helix type polymer (starch), the coiled conformation shields many of the hydroxyl groups, thereby inhibiting alignments and bonding forces.

Eirich(10) pointed out that polyelectrolytes of high charge density may be pulled entirely onto the surface by salt
formations while stiff or oligomeric molecules with reactive end groups may become anchored at one end only. Figure 3 shows some chain depositions at solid-liquid interface.

**Flocculation Mechanisms**

Basically there are three flocculation models: charge neutralization, mosaic patch, and bridging (11-15). These mechanisms of flocculation take place with increasing order of molecular weight of the flocculants. Flocculants with the smallest molecular weight promote flocculation through charge reduction. On the other hand bridging takes place when polymers with molecular weight of one million and more are employed. Patch attraction as proposed by Gregory (11) is an intermediate stage.

**Charge Neutralization**

The charge neutralization theory is based on the reduction of the height of the repulsion energy barriers of the colloidal particles. It can be done either by increasing the frequency of collision or increasing the concentration of ions in the solution.

Williams and Swanson (16) have shown that if the thickness of the double layer is large, it will be very difficult for two surfaces to approach closely enough to allow van der Waals bonding forces to become established. They indicated one way of
Figure 3. Various Models of Macromolecular Chain Deposition at a Solid-Liquid Interface (10). (a) chain totally lying on interface; (b) layer of chains standing on end; (c) partially adsorbed chains (d) chain adsorbed by short sections, with loops of random length extending into solution (e) straight and rigid chains lying flat on interface.
inducing coagulation is to increase the frequency of collision by stirring with greater intensity. Therefore, the approaching forces can overcome the double layer repulsion and allow bonding to take place. The importance of collision was also shown by Stratton (9). Increasing the concentration of ions in the solution had the effect of screening the surface charges from one another by shrinking the double layer thickness and reducing the zeta potential. Coagulants play an important role in this process.

Two types of coagulants are available: inorganics and synthetic organics. Alum and sodium aluminate are typical inorganic coagulants which are effective in acid papermaking systems. The effectiveness of a given salt is governed by the valence of the cation. The Shultz-Hardy rule states that the higher valence of the cation, the more effective the salt in the charge at the surface. An example of this series would be $\text{Al}^{3+} > \text{Mg}^{2+} > \text{Na}^+$. Synthetic organic coagulants are highly cationic, low molecular weight polymers. They usually act through a charge group bearing a quaternary nitrogen, phosphonium, or sulfonium ion. The molecule is flexible enough to bond via charge-charge interaction at many sites along the chain (17).
Bridging

In the bridging mechanism of colloidal aggregation, Heller (21) suggests the polymer molecules adsorb on the particle surface at one or many sites leaving "loops" extending into the bulk solution. The length of individual loops will depend on the free energy of adsorption (22). Large loops will occur when there are few segments adsorbed on the surface with small adsorption free energy. The loops in bulk solution will be able to interact with and adsorb onto other particle surfaces on collision, producing a three dimensional network. (see Figure 4)

Figure 4: Bridging Flocculation: (a) two particles by one polymer molecule; (b) two particles by two separately adsorbed polymer molecules.

The bridging between particles only depends on the ability of the polymer to span the combined electrical
double layers of the particle. Consequently, zero zeta potential is not required for bridging (23). Compression of the double layer by large amounts of electrolyte may inhibit the bridging ability of the polymers because of the reduction in size of the polymer. Lumer and Gossens (24) pointed out the polymer will assume a random coil in solution, and the size will vary with the charge density. The greater the charge density, the more the intramolecular repulsion, thus causing chain extension and a coil with a greater radius of gyration.

Lindquist (25) concluded that for systems having moderately low charges, the dominant flocculation mechanism was polymer bridging. In Stratton’s recent study (9) of a range of polymer degrees of ionization from 3% to 95%, he pointed out when polymer is 3% ionized, polymer bridging was the predominant flocculation mechanism. On the other hand, when charge density was greater than 10%, the flocculation occurred through the patch mechanism.

Mosaic Patch

The patch theory has been extensively studied by Kasper (18). He showed the size of the patch was primarily a function of polymer molecular weight and the total patch area was a function of the amount of polymer absorbed. If too much was added, charge reversion occurred and repulsion resulted as shown in Figure 5.
Gregory (19) postulated the patch mechanism which involves uneven distribution of charges resulting from the adsorption of discrete patches of polymer on the surface. This causes permanent dipoles on the particles, which orientate themselves so they will approach in the right configuration for flocculation.

A further application of the patch model is in conjunction with the bridging effect (20). The sequential addition of low molecular weight cationic material is followed by high molecular weight anionic polymer. The cationic patches adsorb anionic polymers in discrete areas, as shown in Figure 6. The extended anionic polymer chains are then free to bond to a cationic patch on another surface. The tenacious floc that results is very resistant to redispersion, but can cause problems with over-flocculation.

Figure 5: Mosaic Patch Flocculation (18)
Deflocculation Under Hydrodynamic Shear

In modern headboxes controlled turbulence is used to minimize large flocs and optimize formation. The interparticle (fines and filler) attractive forces are weak and are destroyed by comparatively gentle agitation. (5) (6)

Britt (7) has suggested the existence of two types of floc which can be obtained through the use of polyelectrolytes: (1) soft flocs, which are any combination of fiber, fines, and filler that are easily dispersed by low levels of turbulence but can reform to the same extent when the disruptive forces are removed; (2) hard flocs, which have much more resistance to dispersion due to turbulence or shear forces but once broken down will not reform to the same extent.

Figure 6. Adsorption of Discrete Cationic Patches That Serve as Anchors for the Adsorption of Long Anionic Polymer Chains. (20)
Van de Ven and Mason (60) proposed that nearly-equal-sized particles do not flocculate readily under high shear conditions and flocs of such particles are easily dispersed because of the elongational component of turbulent flow. Two particles of very different size, such as a fine and a whole fiber, can form a stable pair at high shear rates in which the small particle rotates around the big particle. Only high molecular weight polymers are able to connect the orbiting fines to fibers to form stable aggregates which are difficult to disperse.

Hubbe (13) compared the levels of shear stress relative to the ability of small particles to remain attached. The results showed polyethylenimine and quaternized polyacrylamide were more than adequate for the shear stress at the foils of a fast machine running at 1000 m/min. Cationic starch was also adequate for the predicated shear on a fast machine, but without any margin for error. Systems with no polyelectrolytes were suitable only for the shear stress on a machine running less than about 700 m/min.

Sikora and Stratton (8) have recently studied the effect of polymer charge density on reflocculation of disrupted flocs. The results showed that with high charge density polymers reflocculation readily occurred, and the final state was identical to that before shearing. This is the behavior to be expected when a patch forming polymer is used. However, shearing the flocs formed by bridging polymers led to irreversible changes, which means the amount of reflocculation is less than the amount of flocculation. This result has been
reconfirmed by other Stratton studies(9). He concluded that reflocculation after extreme turbulence is possible provided that (1) a high charge density, patch-forming retention aid is used, and (2) sufficient time is available. The time will depend on the particle collision rate and, therefore, on the level of turbulence in the recovery zone. He suggested that the point of addition should be so chosen that mixing is maximized. The outlet of a high-shear element such as a fan pump or pressure screen is generally a good point.

Retention Additives

Inorganic Salts

Alum and some other inorganic salts have been shown to reduce the surface charge of fines to encourage flocculation. The order of effectiveness increases with valence. Alum is the most commonly used additive. Depending on pH, the aluminum in solution will have various forms (41). Aluminum salts carry a strong cationic charge in the 4.0 - 5.5 pH range. At high pH (greater than about 5.5) aluminum salts are only very weakly cationic and become much less effective in the retention respect. Alum also has the ability to polymerize to a limited degree through the formation of oligated or oxolated structures. However, the addition of alum will increase the acidity of the paper which can be detrimental to paper permanence and strength (42).
Avery (44) showed that an excessive amount of alum in the headbox reduces the effectiveness of other retention aids. Levels of alum in the headbox as high as 5.0 to 6.0 percent are common because of whitewater recycling, and it was shown by Avery that the soluble alum should be reduced below 0.5 percent to achieve maximum performance from polyacrylamide and cationic starch retention aids.

Crow (67) showed that there were two distinct pH regions for aluminum and polyelectrolyte adsorption. At low pH, only soluble aluminum species were present and both sulfate and chloride aluminum salts reduced the rate and amount of polymer adsorption. At high pH the two aluminum salts formed distinctly different precipitates having very different effects upon polymer adsorption.

Nonionic Polymers

Linke (45) showed that polyacrylamide-based polymers improve retention, and the effectiveness of retention increased with molecular weight. Organic compounds containing hydrogen bonding moieties such as the amide and carboxylic acid group can impart hydrogen bonding between two surfaces (45). Bernal (47) has pointed out an interesting consequence of the fact that the hydrogen bond is stronger than the van der Waals forces but weaker than ionic bonds. In "soft" solids composed of covalent molecules loosely held by van der Waals forces, hydrogen bonding may strengthen and harden the structure.
may explain why hydrogen bonding contributes to retention. However, Tay (48) and Linke (39) point out the main parameter for promoting the retention is molecular weight rather than the hydrogen bonding.

Anionic Polymers

The anionic polymers generally derive their anionic character from carboxyl groups introduced into the polymer chain. The hydroxyl in the carboxyl group will dissociate yielding an anionic charge. The charge density of a given molecule depends on the number of functional groups in the chain and the pH of the solution (49). As stated earlier for the "dual addition" system, the anionic polymer can be adsorbed onto surfaces that have been given cationic properties by pretreatment with alum or with low molecular weight cationic materials, then to form strong flocs.

Cationic Polymers

Cationic polymers have the advantage of being readily adsorbed by the normally negative surfaces encountered in the wet end system, thus eliminating the necessity of using intermediaries such as alum. Cationic charges are generated by introducing sulfonium, phosphonium and tertiary or quaternary ammonium groups onto polymer backbones. The adsorption of cationic polymers is usually explained in terms of charge neutralization or physical adsorption. It has been also
suggested that van der Waals forces, hydrogen bonding or mechanical entrapment play important roles in the retention process (50) (51). However, Strazdins (52) showed that mechanical entrapment is not necessary to explain the irreversibility of polyethyleneimine retention, and the adsorption of cationic polymers primarily occurs through the interplay of electrostatic and purely physical forces.

Tanaka, Tachiki and Sumimoto (53) in study of a number of different cationic polymers showed that the primary factor causing adsorption is charge interaction. The extent of adsorption on pulp fibers varied with the pH, with the optimum adsorption tending to shift toward a higher pH as the basicity of the amino group was increased.

The Measurement of Zeta Potential

The following are some popular methods for measuring zeta potential. Microelectrophoresis is used to measure the velocity of individual particle in a potential gradient. The particles are observed with a microscope through a glass cell and the movement of particles is timed, thereby, measuring the velocity (26). Since only the colloidal portion of the suspension is being measured, it has been argued whether measurement of the fines can represent the behavior of whole system containing large particles such as fibers. Strazdins (28) believed that the fine particles are derived from the large ones and, therefore, should
represent the whole system. On the other hand, Moore (29) found that fines react differently to various additives in the system and will give a zeta potential that is not representative of the whole system. However, this method is widely used in the paper industry because of its relative speed and convenience.

The streaming potential technique is said to be more suited to a laboratory than to a mill application (29). In this system the potential is measured by electrodes, up and downstream (26) of a flowing system through a pad. Since the whole sample is being measured, the zeta potential represents both large and small particles in the paper stock system. However, the disadvantages exist in the necessity for uniform packing of the pad and the time consumed in making the pad and running the tests. Also, Malcolm (30) pointed out that even though the arithmetic average of the zeta potential might be similar for two newsprint furnishes, the details of the distribution might be quite different.

Although the electrophoretic mass transport analysis (EMTA) was originally designed to measure the mobility of concentrated clay slurries, it has been used for pulp fines (31). The advantage of this method, as in streaming potential, is that the whole stock is used in determining mobility. However, the limitations are that particles must be small compared to the opening to the compartment, and their consistency must be
low so that the flow pattern of a particle is not influenced by that of nearby particle (32). This technique works well in laboratory situations when its limitations are taken into account.

Application of Zeta Potential Measurement

Many studies have been carried out to show the effects of zeta potential on retention and drainage. It has been reported (32-34) that the best papermachine operations take place at the isoelectric point-zero zeta potential, where the repulsion forces are minimized. However, this zero zeta potential concept is valid only if the retention is dependent solely on charge neutralization and no bridging reactions or mechanical forces are present. When a bridging or patch mechanism occurs, the overall charge on the material need not be reduced to zero for maximum effectiveness (35-37), since polymer adsorption can occur against a charge barrier. In contrast, studies have shown that very good particulate retention can occur while the system is still on the negative side.

Malcolm (30) showed the zeta potential distribution can be much more useful than the mean zeta potential. While average values are useful in indicating general zeta potential levels, they are unable to describe the complexities of the electrokinetics situations behind the average.

Recent studies done by Chen (35) also indicated that single zeta potential measurement may cause control problems. In his
experiments he proposed the concept of "electrocontrast" which might be able to describe the retention phenomena.

Retention Measurement

Basically two different theories have been advanced to explain retention: a mechanical and a colloidal theory. Although mechanical forces must be taken into account to explain the experimental data available, more emphasis has been placed on the chemical nature of the retention phenomena. The total retention is, however, a combination of both and the relative importance is dependent on the particle size as well as many other factors. Colloidal forces will play a greater role when particles are small, where filtration will be more efficient with large particles (54).

In sheet mold formation of paper retention is affected by both colloidal and mechanical entrapment. However, the low level of turbulence makes this method unreliable for predicting actual paper machine performance. This drawback has resulted in the development and use of the dynamic drainage jar (DDJ) (59), which allows the laboratory investigation of colloidal aspects of retention independent of mat formation. Retention studied by DDJ has been found to decrease exponentially with time, until a steady value is reached in about 20 minutes (65). It appears that in most of the published DDJ procedures, where stirring take place only a small fraction of the stock is exposed to maximum shear (66). Some
other devices (57) (58) are modifications of the dynamic drainage jar. These methods bring a forming force underneath the screen to provide a mat formation. It is said that they can provide more reliable predicative values than the no-mat formation approach.

Recently, Sikora and Stratton (8) studied shear tolerance and reflocculation phenomena in a novel way by using a Hercules Hi-Shear viscometer with the continuous pumping of the sample through a modified cup. Nevertheless, this procedure required "minutes" instead of "seconds", which is the typical fourdrinier paper machine operating time. Also the shear force (turbulence) was supplied by a motor which held a constant rpm for the duration of the test, which does not correlate well with typical paper machine conditions where shear rates changing in different regions at different times. None of the above instruments can continuously reveal dynamic changes. It is obvious that a device which can generate a variable shear rate and change shear in a very short time is required to more closely simulate fines and fillers retention on a papermachine.
CHAPTER III

PRESENTATION OF THE PROBLEM

Review of literature has shown that many studies have been done on the filler and fines retention areas from various angles. In general, the major factors studied included molecular weight and charge of the polymer, hydrodynamic shear, and contact time among components.

Recent studies (8) (18) (39) have confirmed that in the case of high charge density (patch-forming) polymers, reflocculation readily occurred, and following shearing the final state was close to that before shearing. On the other hand, shearing the flocs formed by bridging polymers led to irreversible changes and reduced their ability to reflocculate. Chen (35) showed a significant interaction between charge and molecular weight in developing fines retention. Goulet (56) showed the effect of the molecular weight was negligible at moderate shear levels, and become only possibly significant under high shear conditions. The effect of charge level was more obvious in determining the retention effectiveness of a cationic starch retention aid. Nevertheless, the Chen and Goulet studies were based on indirect and steady measurements through a constant shear device or a zeta potential meter. Thus, their results were unable to reveal the dynamic changes during the various shear conditions, which
occur during actual paper machine operation.

In this study a continuous and direct measurement will be used to monitor polymer behavior in the flocculation, deflocculation, and reflocculation system. Although it was not the purpose of this study to simulate a particular paper machine condition, the experimental sequence of polymer addition and shear rate levels was chosen to simulate closely that of the paper machine. Through a three-way factorial design including molecular weight, charge level and shear, this study will analyze the role of different charge levels and molecular weights of cationic starch in developing flocculation and deflocculation under varying shear conditions.
CHAPTER IV

EXPERIMENTAL

Summary of Experimental Design

The flocculation, deflocculation, and reflocculation of fines and filler was investigated by injecting a series of cationic starches containing different molecular weight and charge levels into a filler-fiber fines system under dynamic shear conditions. A three-way factorial design which included shear, charge level, and molecular weight was used in this study. Experimental conditions were chosen to approximate these commonly found on paper machines.

A modified Hercules viscometer with light device was capable of producing and monitoring dynamic change of the colloidal dispersions. Experimental data were first recorded as continuous curves by a chart recorder. The curves were then transformed to mathematical equations via curve fitting. The slopes and intercepts of the equations were used to study the "rate of change" and "amount of change," respectively.

The objective of this experiment was to study shear, charge level, and molecular weight effects in the flocculation, deflocculation, and reflocculation processes. ANOVA analysis was used to determine the significance of these effects in developing H1, H2, H3, T1, T2, T3, Rf, Rd, and Rr. (Definitions, see p.32)
Experimental Instrument

The instrument used in this study was made by combining a Hercules Hi-Shear viscometer and a Brice Phoenix light scattering spectrophotometer (see Figure 7). The reason for choosing the Hercules viscometer was that it could generate very high shear and the motor itself could accelerate the bob to the selected rpm almost instantaneously. Also the speed of the bob could be changed during testing by means of the variable rpm dial or rpm selector switch. With these functions, it was possible to simulate the shear rate levels of the papermachine forming process on a continuous basis. The spectrophotometer was originally used for light scattering measurement. Some modifications were made to reverse the light source and photocell detector positions, so that they could be more easily adapted to the Hercules system. Also a milliamp meter connected to the spectrophotometer output was used for sensitivity adjustment. Finally, a Hitachi chart recorder was connected to the photocell for recording the experimental light transmission results.

Cup and Bob Design

The cup and bob for the viscometer were made from Lucite (acrylic plastic). The size of the plastic tube and rod were first carefully selected to ensure that only minor modification was needed to adapt them to the existing system. The machined
tube and rod were finally polished to impart better transparency. Polymer solution was injected by a 3 c.c. syringe into the injection port in the lower part of cup. A schematic diagram of the concentric cup apparatus is shown in Figure 8.

![Diagram of Hercules Viscometer](image)

Figure 7: Instrument Design

Shear Apparatus Theory

By assuming the coaxial cup and bob apparatus to be approximated by a parallel plate system (see Fig. 8), the shear rate \( \dot{\gamma} \) (1/sec) at the bob for a rotational velocity \( Q \) (radians/second) is given by

\[
\dot{\gamma} = \frac{2 Q (R_c/R_b)^2}{(R_c/R_b)^2 - 1} \quad \text{(Equation I)}
\]
Figure 8. Schematic Diagram of Cup and Bob
(All dimensions are given in inches)
where $R_c$ and $R_b$ are the radii of cup and bob, respectively.

According to Taylor (55), with the bob rotating inside a stationary cup, the material on the surface of the bob will rotate faster than any other material in the system. Centrifugal force eventually causes a radial migration and finally the onset of flow instability, the $p$ factor. The definition of $p$ is

$$p = \pi v (R_c + R_b) / 2 Q X_0 R_c$$  (Equation II)

where $v$ is the kinematic viscosity ($v = J/\rho$), and $X_0$ is the distance between cup and bob. $J$ is the viscosity in g/cm-s and $\rho$ is the density of the fluid in g/cm$^3$. The factor is correlated to the geometry of the measuring viscometer as

$$p = 0.0571 ((1 + u) / (1 - u) - 0.062 X_0 / R_b) +$$
$$0.00056 [(1 + u) / (1 - u) - 0.652 X_0 / R_b]^{-1}$$  (Equation III)

where $u = \omega_c / \omega_b$, $\omega_c$ and $\omega_b$ are the angular speed of cup and bob, respectively; $u = 0$ for rotating bob and stationary cup. Equation II and III together constitute the conditions for the unstable flow.

The bob used in this study was rotated at 200, 1100, and 2200 rpm, which corresponds to shear rates of 190, 1045, and 2090 1/sec according to equation I. (see Appendix A)

Because of the Taylor vortices phenomena, it is necessary
to calculate the transition rpm for this experiment. The calculations based on equation I, II and III (see Appendix A) showed this rpm was equal to 2580 rpm and 2456 1/sec. This means 200, 1100, and 2200 rpm are in the laminar flow region.

Typical Flocculation, Deflocculation, and Reflocculation Curves

The continuous flocculation, deflocculation, and reflocculation curves were obtained from the instrument as described above. A schematic representation of the curves is shown in Figure 9. The parameters of the curves are defined as follows:

To : Time of injection of flocculant
T1 : Total time of flocculation under low shear S1.
T2 : Total time of deflocculation under high shear S2.
T3 : Total time of reflocculation under low shear S3.
H1 : Maximum amount of flocs generated under low shear S1.
H2 : Amount of flocs retained after high shear S2.
H3 : Maximum amount of reflocculation under low shear S3.
Rf : Initial rate of flocculation (slope of line).
Rd : Initial rate of deflocculation (slope of line).
Rr : Initial rate of reflocculation (slope of line).

The Selection of the Operating RPM and Injection Point

The experimental design included the same low shear rate in zone I and III, and two high shear rates for zone II. The magnitudes of the shear rate were chosen to approximate those commonly found on paper machines.

According to d'Incau (40), the shear rates in the header pipe and on the wire are relatively low, so we arbitrarily choose
Figure 9: Schematic Representing Flocculation, Deflocculation, and Reflocculation Curves.
200 rpm which corresponds to 190 1/sec for zones I (initial flocculation zone after flocculant addition) and III (simulate drainage zone following formation on paper machine).

On the other hand, the shear rates in the paper machine headbox are extremely high (in the range of 10 to 10 $^3$ 1/sec) (41). Therefore, 1100 and 2200 rpm for zone II were selected. The shear rates were 1045 and 2090 1/sec, respectively, which approximate the range of shear generated in the headbox of paper machines running in the 1000 to 3000 fpm range. (Appendix E)

Because the initial shear rate used was low (190 1/sec), special care was needed to provide good mixing. The injection point was carefully selected and drilled in the lower portion of the cup. The diluted polymer was immediately injected with a high momentum by a 3 c.c. syringe to ensure quick and uniform polymer distribution into the suspension. A preliminary test, using a red ink injection into water, revealed that the time required to achieve uniform mixing by this method was rather short. In Figure 10 the time, $t$, was about 0.1 seconds.

The Duration of Flow Under Shear

It is obvious that the residence times of particles in various regions of a paper machine system vary considerably from one location to another and strongly depend on the machine geometry. However, a fluid in a pump or headbox will experience a high shear rate for a very short time, e.g., 1 to 3
milliseconds. A fluid will experience a low shear rate for a much longer time in the pipes and forming zones depending on the pipe and forming zone length and fluid velocity. These variations of time and level of shear rate can make a significant difference on degree of flocculation, deflocculation, and reflocculation. Stratton (9) pointed out 10 to 40 seconds may be required to reach maximum retention for a TiO$_2$ and polymer system, however the times for total deflocculation and reflocculation were not investigated. Consequently, it is necessary to apply predefined time and shear levels for every experiment in this study.

To determine the time intervals for this study, a medium molecular weight and medium charge starch solution was injected into a fines-clay suspension under 200-1100-200 rpm bob rotation. The best results were obtained by using 40-5-40 seconds, where 40 seconds was enough for developing maximum flocculation and reflocculation, and 5 seconds was capable of breaking down the flocs to reach an equilibrium deflocculated
state. Thus, this sequence of times was maintained constant for all experiments.

The experimental conditions of shear and time for the various zones are summarized in Table 1. The light intensity was constant throughout all experiments. The sensitivity of the photocell was adjusted with gain control to achieve full scale readings of 0 to 10 mA. Data could be read from the chart recorder. It should be mentioned that all the readings were based on the original sample which was read 5.0 mA and used as a "zero" basis in this study. For example, the amount of flocculation (H1) for HMW-LC cationic starch was read 1.1 mA based on the original sample. The actual reading was 3.9 mA (5.0 mA - 1.1 mA = 3.9 mA) and can be converted to 0.77 in turbidity. (see Appendix G)

Table 1

<table>
<thead>
<tr>
<th>Summary of Experimental Variables</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ZONE I</strong></td>
</tr>
<tr>
<td>Shear Rate (1/s)</td>
</tr>
<tr>
<td>(rpm)</td>
</tr>
<tr>
<td>Time (sec)</td>
</tr>
</tbody>
</table>
Experimental Methods and Materials

**Fines-Clay Suspension**

Hardwood fines and Klondike filler clay were used for all experiments. Weyerhaeuser hardwood kraft fibers were refined to 300 CSF using a laboratory Valley beater. A Britt dynamic drainage jar was used to collect the fines which passed a 75 micron diameter screen perforation. Because of high hardness of the tap water, distilled water was used to wash the fines. A 0.12% total solids suspension was prepared containing 0.08% fiber fines and 0.04% filler clay. This suspension was adjusted to pH 4.5 and used for all experimentation. The detailed preparation method is listed in Appendix B.

**Cationic Starch Solution**

Cationic starch differs according to parent starch source, substituent groups, degree of substitution, distribution of cationic groups and molecular size and shape. The extent of cationization in cationic starch is equivalent to the degree of substitution (Appendix C). Table 2 gives the nine cationic waxy maize starches which were used in this study. These starches were prepared by Richard Harvey, Grain Processing Corporation, Muscatine, Iowa.

The high molecular weight level starch was unmodified waxy maize. The lower molecular weights was obtained by alkaline
ammonium persulfate catalyzed hydrolysis (Appendix C). The three molecular weight and charge levels chosen provided a wide range to study. The amount of 0.5g of each starch was first heated to 195°F for 40 minutes in 800 ml distilled water. The starch solutions were stored in sealed bottles to prevent contamination. All starch solutions were used within 48 hours to minimize changes during storage.

**Statistical Design**

The experimental variables were chosen close to typical paper machine operating conditions, except that longer times were used (40-5-40 seconds) to assure equilibrium in each zone, to give better resolution of the results, and also to more easily control the instrument.

An experimental design which included shear, charge level, and molecular weight was selected using the 3 x 3 x 2 factorial design with 4 replicates in each cell as listed in Table 3. In each cell there are four, four-digit numbers. The first digit

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>High</th>
<th>Medium</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of</td>
<td>0.0140</td>
<td>0.0130</td>
<td>0.0136</td>
</tr>
<tr>
<td>substitution</td>
<td>0.0307</td>
<td>0.0328</td>
<td>0.0325</td>
</tr>
<tr>
<td></td>
<td>0.0833</td>
<td>0.0883</td>
<td>0.0852</td>
</tr>
</tbody>
</table>
(1 or 2) indicates the levels of high shear employed (1100 or 2200 rpm). The second digit (1 or 2 or 3) indicates the levels of the starch molecular weight employed (1 is low, 2 is medium, and 3 is high). The third digit (1 or 2 or 3) indicates the magnitude of the starch's charge (1 is low, 2 is medium, and 3 is high). The fourth digit (1 or 2 or 3 or 4) indicates the replicate in this cell. Replicates 1 and 2 were collected using a normal speed recorder; 3 and 4 were collected with a high speed recorder.

Table 3

<table>
<thead>
<tr>
<th>Statistical Experimental Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
</tr>
<tr>
<td>Charge level</td>
</tr>
<tr>
<td>Hi-Shear level 1100 rpm</td>
</tr>
<tr>
<td>1112</td>
</tr>
<tr>
<td>1113</td>
</tr>
<tr>
<td>1114</td>
</tr>
<tr>
<td>Hi-Shear level 2200 rpm</td>
</tr>
<tr>
<td>2112</td>
</tr>
<tr>
<td>2113</td>
</tr>
<tr>
<td>2114</td>
</tr>
</tbody>
</table>

* Two high shear levels (1100, 2200 rpm) were used in shear zone II; 200 rpm was used in shear zones I and III for all experiments.
The nine kinds of cationic starches will be referred to as follows in the remainder of this report.

- **HMW-HC**: high molecular weight, high charge
- **HMW-MC**: high molecular weight, medium charge
- **HMW-LC**: high molecular weight, low charge
- **MMW-HC**: medium molecular weight, high charge
- **MMW-MC**: medium molecular weight, medium charge
- **MMW-LC**: medium molecular weight, low charge
- **LMW-HC**: low molecular weight, high charge
- **LMW-MC**: low molecular weight, medium charge
- **LMW-LC**: low molecular weight, low charge

A 0.3 ml sample of a 0.06% cationic starch (0.00018 g) was injected into 10 ml of fines and filler suspension (0.008 g fines, 0.004 g filler) in each experiment. Thus, the add-on level of starch was 1.5% based on the weight of total solids of fines plus filler.

**Data Management and Curve Fitting**

After all the experiments were done, curve fitting via regression analysis was used to convert each continuous curve obtained from the chart recorder into a mathematical expression. Thus, in each experiment three equations were obtained to represent flocculation, deflocculation, and reflocculation curves respectively. The procedure used to obtain these equations is listed below:

1. Each curve was converted to a series of points \((X_1, Y_1), (X_2, Y_2), ..., (X_n, Y_n)\), where \(X_1, X_2, ..., X_n\) represent time intervals, and \(Y_1, Y_2, ..., Y_n\) represent mA which was read based on the original sample. "mA" can be converted to turbidity based on the method introduced in...
Appendix G. The number of points, n, was 50 for flocculation and deflocculation curves, and 60 for deflocculation curves. Because of the numerous data points generated by this step, a computer program was written for data handling. (Appendix F)

2. Regression analysis was used to simulate those points during the estimation. The quadratic models were used to achieve a 95% coefficient of determination.

3. To draw a curve which represented four replicated runs, the data points obtained in procedure 1 for each set of four runs were averaged to produce a new series of points. The "mean" equation was obtained via curve fitting based on these new generated points.
   (the final equations are listed in Appendix D)

Experimental curves were then redrawn based on the equations obtained from procedure 3. The completed set of flocculation, deflocculation, and reflocculation curves for this study is given in Appendix G.
CHAPTER V

PRESENTATION OF RESULTS AND DISCUSSION

The following analysis is designed to illustrate the flocculation phenomena caused by adding cationic starch, with three levels of charge and molecular weight under varying shear conditions. The statistical analysis of this study was accomplished by analysis of variance, where either two-way or three-way was used depending on the number of variables under study.

All of the original data obtained for this study are presented in Appendix H.

Amount of Flocculation

The amount of flocculation of fines and filler, given in Table 4, demonstrates the maximum amount of flocs generated at low shear (H1, Figure 9) caused by adding cationic starch of different molecular weight and charge at 200 rpm bob rotation in 40 seconds.

The figures in each cell are an average relative turbidity of four experiments. (The method of converting mA to turbidity is listed in Appendix G). Upon deflocculation, the decrease of partial size produced decreased in turbidity.

The two way ANOVA analysis, given in the Table 5, was used to study the main effects (charge or molecular
weight), and interaction effects (charge and molecular weight). A Welch pairwise comparison (64) was performed to compare the differences of flocculation in each cell, caused by either the main or interaction effects. Results are shown in Table 6.

Table 4

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>20.5 (1)</td>
<td>24.0 (2)</td>
<td>35.0 (3)</td>
</tr>
<tr>
<td>Medium</td>
<td>5.0 (4)</td>
<td>13.0 (5)</td>
<td>25.0 (6)</td>
</tr>
<tr>
<td>Low</td>
<td>2.5 (7)</td>
<td>9.0 (8)</td>
<td>22.0 (9)</td>
</tr>
</tbody>
</table>

(Unit: x0.05mA)
*Numbers 1 to 9 in parentheses in Table 4 was used to identify "group - group" of Welch pairwise comparison. (see Table 6)

From Table 4 and 5, it can be seen that both charge and molecular weight significantly affected the amount of flocculation at the 5% level of significance. This significant effect was also found for the interaction term (charge - molecular weight). By comparing the magnitude of each cell in Table 4, it is obvious that the highest flocculation was generated by adding HMW-HC cationic starch, and the lowest flocculation was caused by adding LMW-LC cationic starch.
Table 5

Least Squares ANOVA Molecular Weight and Charge Effects on the Amount of Flocculation (H1)

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell</td>
<td>8</td>
<td>1739.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>753.08</td>
<td>376.54</td>
<td>1936.50</td>
<td>0.000</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>960.58</td>
<td>480.29</td>
<td>2470.07</td>
<td>0.000</td>
</tr>
<tr>
<td>Charge-Molecular Wt</td>
<td>4</td>
<td>26.08</td>
<td>6.52</td>
<td>33.54</td>
<td>0.000</td>
</tr>
<tr>
<td>Within</td>
<td>9</td>
<td>1.75</td>
<td>0.19</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

From Table 6, it can be seen that there were four cationic starches (HMW-LC, HMW-MC, MMW-HC, and LMW-HC) which had no significant differences in developing flocculation at the 5% level of significance (Appendix I). Consequently, we can conclude the following decreasing trend of the nine cationic starches in developing amount of flocculation:

\[
\text{HMW-LC} > \text{HMW-HC} > \text{HMW-MC} > \text{MMW-LC} > \text{MMW-MC} > \text{MMW-HC} > \text{LMW-MC} > \text{LMW-LC} > \text{LMW-HC}
\]

From the above comparison, the different amounts of flocculation generated by HMW-LC, MMW-LC, and LMW-LC largely were due to the difference of molecular weight. However this molecular weight effect can not be used to explain the same amount of flocs generated by the four different cationic starches grouped as shown above. The reason for this similar floc generation is probably due to the effects of charge on the starch molecules.
Table 6

Welch Pairwise Comparison of H1 Among Nine Kinds of Cationic Starches

<table>
<thead>
<tr>
<th>*Group-Group</th>
<th>T-Value</th>
<th>DF</th>
<th>PROB</th>
<th>MEAN DIF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 2</td>
<td>-8.485</td>
<td>2</td>
<td>0.014</td>
<td>-3.000</td>
</tr>
<tr>
<td>1 3</td>
<td>-24.597</td>
<td>1</td>
<td>0.026</td>
<td>-13.750</td>
</tr>
<tr>
<td>1 4</td>
<td>63.000</td>
<td>1</td>
<td>0.010</td>
<td>15.750</td>
</tr>
<tr>
<td>1 5</td>
<td>21.213</td>
<td>2</td>
<td>0.002</td>
<td>7.500</td>
</tr>
<tr>
<td>1 6</td>
<td>-8.708</td>
<td>1</td>
<td>0.094</td>
<td>-3.750</td>
</tr>
<tr>
<td>1 7</td>
<td>50.912</td>
<td>2</td>
<td>0.000</td>
<td>18.000</td>
</tr>
<tr>
<td>1 8</td>
<td>32.527</td>
<td>2</td>
<td>0.001</td>
<td>11.500</td>
</tr>
<tr>
<td>1 9</td>
<td>-4.243</td>
<td>2</td>
<td>0.051</td>
<td>-1.500</td>
</tr>
<tr>
<td>2 3</td>
<td>-19.230</td>
<td>1</td>
<td>0.033</td>
<td>-10.750</td>
</tr>
<tr>
<td>2 4</td>
<td>75.000</td>
<td>1</td>
<td>0.008</td>
<td>18.750</td>
</tr>
<tr>
<td>2 5</td>
<td>29.698</td>
<td>2</td>
<td>0.001</td>
<td>10.500</td>
</tr>
<tr>
<td>2 6</td>
<td>-1.346</td>
<td>1</td>
<td>0.408</td>
<td>-0.750</td>
</tr>
<tr>
<td>2 7</td>
<td>59.397</td>
<td>2</td>
<td>0.000</td>
<td>21.000</td>
</tr>
<tr>
<td>2 8</td>
<td>41.012</td>
<td>2</td>
<td>0.001</td>
<td>14.500</td>
</tr>
<tr>
<td>2 9</td>
<td>4.234</td>
<td>2</td>
<td>0.051</td>
<td>1.500</td>
</tr>
<tr>
<td>3 4</td>
<td>59.000</td>
<td>1</td>
<td>0.011</td>
<td>29.500</td>
</tr>
<tr>
<td>3 5</td>
<td>38.013</td>
<td>1</td>
<td>0.017</td>
<td>21.250</td>
</tr>
<tr>
<td>3 6</td>
<td>14.142</td>
<td>2</td>
<td>0.005</td>
<td>10.000</td>
</tr>
<tr>
<td>3 7</td>
<td>56.796</td>
<td>1</td>
<td>0.011</td>
<td>31.750</td>
</tr>
<tr>
<td>3 8</td>
<td>45.169</td>
<td>1</td>
<td>0.014</td>
<td>25.250</td>
</tr>
<tr>
<td>3 9</td>
<td>21.913</td>
<td>1</td>
<td>0.029</td>
<td>12.250</td>
</tr>
<tr>
<td>4 5</td>
<td>-33.000</td>
<td>1</td>
<td>0.019</td>
<td>-8.250</td>
</tr>
<tr>
<td>4 6</td>
<td>-39.000</td>
<td>1</td>
<td>0.016</td>
<td>-19.500</td>
</tr>
<tr>
<td>4 7</td>
<td>9.000</td>
<td>1</td>
<td>0.007</td>
<td>2.250</td>
</tr>
<tr>
<td>4 8</td>
<td>-17.000</td>
<td>1</td>
<td>0.037</td>
<td>-4.250</td>
</tr>
<tr>
<td>4 9</td>
<td>-69.000</td>
<td>1</td>
<td>0.009</td>
<td>-17.250</td>
</tr>
<tr>
<td>5 6</td>
<td>-20.125</td>
<td>1</td>
<td>0.032</td>
<td>-11.250</td>
</tr>
<tr>
<td>5 7</td>
<td>29.698</td>
<td>2</td>
<td>0.001</td>
<td>10.500</td>
</tr>
<tr>
<td>5 8</td>
<td>11.314</td>
<td>2</td>
<td>0.008</td>
<td>4.000</td>
</tr>
<tr>
<td>5 9</td>
<td>-25.456</td>
<td>2</td>
<td>0.002</td>
<td>-9.000</td>
</tr>
<tr>
<td>6 7</td>
<td>38.908</td>
<td>1</td>
<td>0.016</td>
<td>21.750</td>
</tr>
<tr>
<td>6 8</td>
<td>27.280</td>
<td>1</td>
<td>0.023</td>
<td>15.250</td>
</tr>
<tr>
<td>6 9</td>
<td>4.025</td>
<td>1</td>
<td>0.155</td>
<td>2.250</td>
</tr>
<tr>
<td>7 8</td>
<td>-18.385</td>
<td>2</td>
<td>0.003</td>
<td>-6.500</td>
</tr>
<tr>
<td>7 9</td>
<td>-55.154</td>
<td>2</td>
<td>0.000</td>
<td>-19.500</td>
</tr>
<tr>
<td>8 9</td>
<td>-36.770</td>
<td>2</td>
<td>0.001</td>
<td>-13.000</td>
</tr>
</tbody>
</table>

*See note below Table 4.
where the high intramolecular repulsion force will expand the molecular coils, and thus, expose more surface area for increased flocculation. This is why LMW-HC can promote the second best flocculation performance although it is lowest in molecular weight. Finally, it is suggested that molecular weight and charge cannot solely explain the flocculation phenomena and that both parameters must be considered together.

Amount of the Flocs Retained after Deflocculation Process (H2)

Two levels of high shear (1100 and 2200rpm) were used to generate a three way ANOVA analysis with three levels of molecular weight and charge of cationic starch. The amount of flocs retained after introducing high shear for 5 seconds (H2) is given in Table 7, where the positive values mean the high shear was unable to break down all the flocs generated in the previous stage (Zone I). The negative values mean the high shear not only broke down all the flocs generated in zone I, but also broke down aggregates present in the original sample. This phenomena showed that some flocs had formed before the cationic starch was added. Since the original state was not totally deflocculated, an absolute comparison in this study was impossible to perform. However by arbitrarily choosing the initial state (at time = To) as a zero basis of flocculation, the analyses of this study could then be performed.

From the Table 7, it is found that the two levels of high
shear generated different degrees of deflocculation, except for
the LMW-LC cationic starch where increasing shear did not
increase deflocculation. This is probably explained by the
charge neutralization mechanism in which flocs have low shear
resistance and are very easily broken down. The flocs in all of
the rest of the experiments were probably formed by a bridging
condition, which was more resistant to breakdown so the low shear
levels caused less deflocculation than the high shear.

Table 7
Amount of Flocs Retained Under
1100 and 2200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge level</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1100 rpm</td>
<td>-5.0</td>
<td>-1.0</td>
<td>2.0</td>
</tr>
<tr>
<td>2200 rpm</td>
<td>-5.0</td>
<td>-3.5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

(unit: x0.05mA, height of H2, Figure 9)

From Table 8, it is found that flocs were totally broken
down under 2200 rpm except HMW-HC flocs. Under 1100 rpm, high-
charged flocs resisted breaking down in all three molecular
weight levels.
Table 8
Amount of Flocs (%) Resistant to Shear Breakdown
Under 1100 and 2200 rpm (1 - H2/H1)

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge level</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Shear</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200rpm</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>1100rpm</td>
<td>0.0</td>
<td>0.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

(Unit: %)

Table 9
Analysis of Variance:
Molecular Weight, Charge, and Shear Affect the Amount of the Flocs Retained

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subclasses</td>
<td>240.13</td>
<td>17</td>
<td>14.13</td>
<td>11.300</td>
<td>0.015</td>
</tr>
<tr>
<td>A</td>
<td>10.13</td>
<td>1</td>
<td>10.13</td>
<td>8.100</td>
<td>0.047</td>
</tr>
<tr>
<td>B</td>
<td>106.08</td>
<td>2</td>
<td>53.04</td>
<td>42.433</td>
<td>0.002</td>
</tr>
<tr>
<td>C</td>
<td>81.08</td>
<td>2</td>
<td>40.54</td>
<td>32.433</td>
<td>0.003</td>
</tr>
<tr>
<td>AB</td>
<td>22.75</td>
<td>2</td>
<td>11.38</td>
<td>9.100</td>
<td>0.032</td>
</tr>
<tr>
<td>AC</td>
<td>9.75</td>
<td>2</td>
<td>4.88</td>
<td>3.900</td>
<td>0.115</td>
</tr>
<tr>
<td>BC</td>
<td>5.33</td>
<td>4</td>
<td>1.33</td>
<td>1.067</td>
<td>0.476</td>
</tr>
<tr>
<td>ABC</td>
<td>5.00</td>
<td>4</td>
<td>1.25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(A: shear; B: molecular weight; C: charge)

From the Table 9 it can be seen that molecular weight, charge, and shear all significantly affected the amount of...
deflocculation at the 5% level of significance. Shear does not appear as significant as molecular weight and charge. The interaction term (shear-molecular weight) is significant at the 5% level of significance while shear-charge is significant at the 25% level of significance, indicating a mild interaction between shear and charge, and a slightly higher interaction between shear and molecular weight. The results are in agreement with Mason and van de Ven study (60), which illustrated that colloidal forces play only a minor role when suspensions are subjected to high shear and the molecular weight is more responsible than charge level in imparting shear resistant characteristics to flocs. From the Table 7, it can be seen that flocs formed by high molecular weight polymer cannot easily be broken up by high shear and are more resistant to breakdown than low molecular weight ones. Mason also pointed out that aggregates of equal-sized particles are easier to break up than aggregates of unequal-sized particles when subjected to the same hydrodynamic forces. With respect to this point, it should be noted that in this study the particle size of the fiber fines was in the range of 15 to 100 µ and the average size of the filler clay was 3 µ. It is expected that some flocs formed by clay and large fiber fines particles with high

*Laboratory SEM analysis of fines and filler clay were performed at Western Michigan University by Deepak Bhargava.
molecular weight starches would probably be retained under high shear forces, and the results from Table 7 are in agreement with this relative-particle-sized concept. Finally, the results showed there was no significant effect for the charge-molecular weight interaction term.

Amount of Reflocculation (H3)

After applying high shear for 5 seconds, the amount of reflocculation was measured after 200 rpm bob rotation for a time of 40 seconds. The amount of reflocculation of fines and filler is given in Table 10, and the three way AOV table is given in Table 11.

Table 10

The Amount of Reflocculation in Systems Containing Nine Kinds of Cationic Starches Following 1100 and 2200 rpm (Units in table are milliamps which can be converted to turbidity by the method listed in Appendix H)

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Charge level</th>
<th>LowMedium</th>
<th>Medium</th>
<th>High</th>
<th>LowMedium</th>
<th>High</th>
<th>Shear</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
<td>2200 rpm</td>
<td>1.0</td>
<td>6.0</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td>1100 rpm</td>
<td>1.0</td>
<td>6.0</td>
<td>12.0</td>
<td>1.5</td>
<td>6.5</td>
<td>13.0</td>
<td>14.0</td>
<td>13.5</td>
<td>21.5</td>
</tr>
</tbody>
</table>

(Unit: x0.05 mA)

From Table 10, it can be seen that 1100 rpm affected the flocs less so they showed a little higher reflocculation than following 2200 rpm. However, the amount of flocs increased
by this effect seemed rather small. The high molecular weight systems gave the largest difference between the two shear levels. At low and medium molecular weight, only the highest charged starches showed a difference in reflocculation following high vs. low shear.

From Table 11, the three way ANOVA showed the molecular weight, charge, and shear all significantly affected the amount of reflocculation at the 5% level of significance. Both shear-molecular weight and shear-charge interactions were only significant at the 25% level of significance, indicating little interaction. However, molecular weight-charge interaction was highly significant at the 5% level of significance, indicating a large interaction between molecular weight and charge in promoting reflocculation.

Since the suspensions were measured at the same conditions (40 seconds and 200 rpm bob rotation) before and after high shear, the percentage of floc recovery after high shear could be calculated (H3/H1, Figure 9, p.33). Table 12 give the results and the three way AOV based on these results is given in the Table 13.

From Table 12 it can be seen that none of the cationic starch gave 100% reflocculation. However, more than 50% flocs can be recovered in most cases except for LMW-LC and MMW-LC. This study suggested that the flocculation mechanisms were more like the bridging process.
Table 11
Analysis of Variance:
Molecular Weight, Charge, and Shear Effects on the Amount of Reflocculation

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subclasses</td>
<td>664.28</td>
<td>17</td>
<td>39.08</td>
<td>401.904</td>
<td>0.000</td>
</tr>
<tr>
<td>A</td>
<td>1.39</td>
<td>1</td>
<td>1.39</td>
<td>14.285</td>
<td>0.019</td>
</tr>
<tr>
<td>B</td>
<td>349.78</td>
<td>2</td>
<td>174.89</td>
<td>1798.802</td>
<td>0.000</td>
</tr>
<tr>
<td>C</td>
<td>294.69</td>
<td>2</td>
<td>147.35</td>
<td>1515.525</td>
<td>0.000</td>
</tr>
<tr>
<td>AB</td>
<td>0.44</td>
<td>2</td>
<td>0.22</td>
<td>2.286</td>
<td>0.218</td>
</tr>
<tr>
<td>AC</td>
<td>0.53</td>
<td>2</td>
<td>0.26</td>
<td>2.714</td>
<td>0.180</td>
</tr>
<tr>
<td>BC</td>
<td>17.06</td>
<td>4</td>
<td>4.26</td>
<td>43.856</td>
<td>0.001</td>
</tr>
<tr>
<td>ABC</td>
<td>0.39</td>
<td>4</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(A: shear; B: molecular weight; C: charge)

Table 12
Percentage of Floc Recovery for Systems Containing Nine Kinds of Cationic Starch Following 1100 and 2200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Floc recovery, %</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge level</td>
<td>Low Medium High</td>
<td>Low Medium High</td>
<td>Low Medium High</td>
<td>Low Medium High</td>
</tr>
<tr>
<td>Shear</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200 rpm</td>
<td>30 66 50</td>
<td>30 50 48</td>
<td>61 54 59</td>
<td></td>
</tr>
<tr>
<td>1100 rpm</td>
<td>30 66 55</td>
<td>30 50 52</td>
<td>68 56 61</td>
<td></td>
</tr>
</tbody>
</table>

(% = amount of reflocculation/ amount of flocculation x 100, (H3/H1) x 100)
Table 12 also shows that floc recovery was good (54-68%) for all charge levels of high molecular weight starch. In the case of medium and low molecular weight starch, low charge level was relatively ineffective and either medium or high charge was needed to get good recovery of flocs.

Table 13

Table 13 shows that charge and molecular weight were significant at the 5% level of significance, and this significant effect also can be found in their interaction term. The other effects were not significant at either the 5% or 25% level of significance, indicating the % of recovered flocs was strongly affected by charge and molecular weight and that shear

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subclasses</td>
<td>2829.78</td>
<td>17</td>
<td>166.46</td>
<td>43.741</td>
<td>0.001</td>
</tr>
<tr>
<td>A</td>
<td>22.22</td>
<td>1</td>
<td>22.22</td>
<td>5.839</td>
<td>0.073</td>
</tr>
<tr>
<td>B</td>
<td>834.11</td>
<td>2</td>
<td>417.06</td>
<td>109.592</td>
<td>0.000</td>
</tr>
<tr>
<td>C</td>
<td>817.44</td>
<td>2</td>
<td>408.72</td>
<td>107.402</td>
<td>0.000</td>
</tr>
<tr>
<td>AB</td>
<td>4.78</td>
<td>2</td>
<td>2.39</td>
<td>0.628</td>
<td>0.579</td>
</tr>
<tr>
<td>AC</td>
<td>6.78</td>
<td>2</td>
<td>3.39</td>
<td>0.891</td>
<td>0.479</td>
</tr>
<tr>
<td>BC</td>
<td>1129.22</td>
<td>4</td>
<td>282.31</td>
<td>74.183</td>
<td>0.001</td>
</tr>
<tr>
<td>ABC</td>
<td>15.22</td>
<td>4</td>
<td>3.81</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(A: shear; B: molecular weight; C: charge)
level prior to recovery was not a significant effect.

According to van de Ven (63), at high shear rates the possibility exists that rupture of the polymer chain occurs or that the polymer will be torn off the surface of one of the particles. The force required to break a carbon-carbon bond in a polymer chain is of the order of 1 to 10 nN. In the case of two particles of radii $a_1$ and $a_2$, the hydrodynamic force at short distances equals:

$$F_{\text{hydr}} = 19.2 G a_1 a_2 \sin \theta \sin 2\phi$$

$G$ being the rate of shear, $\gamma$ the viscosity of the suspending medium, and $\theta$ and $\phi$ polar angles describing the relative orientation of the spheres in shear flow. When $a_1 = 20 \mu$, $a_2 = 3.0 \mu$ for fines and clay, respectively, and $G = 2090$ 1/s (2200 rpm), this force equals 2.4 nN at the orientation at which $\sin \theta \times \sin 2\phi = 1$. This force is about the magnitude needed to break carbon-carbon bonds. Since fines particles are in the range of 100 to 15 \mu. This means that degradation of starches can occur in most cases. This explain why complete recovery of flocs was not possible in these experiments.

A Detailed Analysis of the Deflocculation Curve

The deflocculation curves obtained from the high speed recorder for the nine cationic starches are listed in Figure 11. It can be seen that some curves can not be treated solely as quadratic or cubic models because the initial part of these
curves are more like a linear line rather than a curve. Figure 12 was used to illustrate this phenomenon and define the new variables for further study.

From Figure 12, the upper curve was separated into three parts: a linear line (I), a transition zone, and a curve (II). The definitions of these variables are listed below. The lower curve (III) represented the low shear resistant flocs.

- \( R_d \): initial rate of deflocculation based on line I
- \( R_d' \): second rate of deflocculation based on curve II
- \( t_1 \): total time of linear behavior during the deflocculation
- \( t_2 \): total time to achieve the equilibrium state (total deflocculation)

The linear behavior (line I) was seen after adding HMW-LC, HMW-MC, HMW-HC, and MMW-HC starches (a, b, c, f in Figure 11). In this study, it was found that \( t_1 \) was equal to about 0.3 second, and the \( R_d' \) was arbitrarily defined at the time equal to 0.5 second. Longer \( t_1 \) represented flocs having a higher shear-resistance.

The linear behavior of deflocculation curves indicates that initial floc break-down is minimal. This may be due to the compression and shielding effect (Figure 13) of the flocs which means some flocs existing outside of the main floc structure will be separated under direct impact of the high shear. However the majority of the inside particles will still stick together to form a compact structure. The shielding effect will no longer exist when enough particles have been pulled off from the main
Figure 11* Detailed Analysis of Deflocculation Curves (a) HMW-LC; (b) HMW-MC; (c) HMW-HC cationic starch
Figure 11 (continued). Detailed Analysis of Deflocculation Curves
(d) MMW-LC; (e) MMW-MC; (f) MMW-HC
cationic starch
Figure 11 (continued): Detailed Analysis of Deflocculation Curves

(g) LMW-LC; (h) LMW-MC; (i) LMW-HC
cationic starch

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Figure 12* Linear Behavior of Deflocculation Curve
Figure 13: Ideal Model for Compression and Shielding Effects
floc structure. Then, high shear will have an impact on each particle and the flocs then will be randomly broken up (68). It should be mentioned that linear behavior was not observed for the relatively compact floc structure formed by LMW-HC cationic starch during the deflocculation process, although it generated a high amount of flocculation.

The Time to Achieve Equilibrium State in Deflocculation Process

The times \((t_2)\) required to achieve equilibrium states of deflocculation are given in Table 14. It shows the flocs generated by HMW-HC had the highest shear resistance, and the flocs generated by LMW-LC had the lowest shear resistance.

Table 14

The Time Required to Achieve Equilibrium Deflocculation of Nine Kinds of Cationic Starches Under 1100 and 2200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge level</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200rpm</td>
<td>1.1</td>
<td>2.0</td>
<td>3.0</td>
<td>1.7</td>
<td>2.2</td>
<td>3.6</td>
<td>2.3</td>
<td>3.3</td>
<td>4.5</td>
</tr>
<tr>
<td>1100rpm</td>
<td>1.9</td>
<td>2.4</td>
<td>3.9</td>
<td>2.6</td>
<td>2.8</td>
<td>4.4</td>
<td>3.0</td>
<td>4.2</td>
<td>4.9</td>
</tr>
</tbody>
</table>

(unit: seconds)

The three way ANOVA based on the data of Table 14 is given in Table 14 and shows that molecular weight, charge, and shear were all significant effects at the 5% level of significance.
The interaction terms were all non-significant at the 25% level of significance. Charge was the most significant factor in controlling the time needed for deflocculation.

Table 15

Analysis of Variance:
Molecular Weight, Charge, and Shear Effects on the Time of Total Deflocculation

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subclasses</td>
<td>13500.94</td>
<td>17</td>
<td>794.17</td>
<td>9.439</td>
<td>0.021</td>
</tr>
<tr>
<td>A</td>
<td>1701.39</td>
<td>1</td>
<td>1701.39</td>
<td>20.221</td>
<td>0.011</td>
</tr>
<tr>
<td>B</td>
<td>3158.11</td>
<td>2</td>
<td>1579.06</td>
<td>18.767</td>
<td>0.009</td>
</tr>
<tr>
<td>C</td>
<td>8081.44</td>
<td>2</td>
<td>4040.72</td>
<td>48.024</td>
<td>0.002</td>
</tr>
<tr>
<td>AB</td>
<td>14.78</td>
<td>2</td>
<td>7.39</td>
<td>0.088</td>
<td>0.918</td>
</tr>
<tr>
<td>AC</td>
<td>70.78</td>
<td>2</td>
<td>35.39</td>
<td>0.421</td>
<td>0.683</td>
</tr>
<tr>
<td>BC</td>
<td>137.89</td>
<td>4</td>
<td>34.47</td>
<td>0.410</td>
<td>0.796</td>
</tr>
<tr>
<td>ABC</td>
<td>336.56</td>
<td>4</td>
<td>84.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(A: shear; B: molecular weight; C: charge)

To further study the charge and molecular weight effects, a 5% protected LSD test (64) was performed. The two way ANOVA for 1100 and 2200 rpm are given in table 16 and 17. The results show that under 2200 rpm, charge and molecular weight were all significant at the 5% level of significance. The relative ability of the starches to form the high-shear-tolerant flocs were in the order:

HMW > MMW = LMW and HC > MC > LC
On the other hand, the results showed that under 1100rpm there were no differences in the effect of molecular weight level on promoting high shear tolerance flocs (HMW = MMW = LMW), but the charge levels did exhibit significant differences:

\[ HC > MC = LC \]

<p>| Table 16 |
| Least Squares ANOVA Molecular Weight and Charge Effects on the Time for Total Deflocculation Under 2200 rpm |</p>
<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>6456.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>1800.67</td>
<td>900.33</td>
<td>80.63</td>
<td>0.001</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>4610.67</td>
<td>2305.33</td>
<td>206.45</td>
<td>0.000</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>44.67</td>
<td>11.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>6456.00</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<p>| Table 17 |
| Least Squares ANOVA Molecular Weight and Charge Effects on the Time for Total Deflocculation Under 1100 rpm |</p>
<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>5343.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>1372.22</td>
<td>686.11</td>
<td>6.39</td>
<td>0.057</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>3541.56</td>
<td>1770.78</td>
<td>16.48</td>
<td>0.012</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>429.78</td>
<td>107.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>5343.56</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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The Time to Achieve Equilibrium State in Flocculation and Reflocculation Processes

The times in seconds to achieve equilibrium states of flocculation and reflocculation are given in Table 18. It can be seen that more time was required for HMW-HC than for LMW-LC cationic starch to achieve equilibrium state in the flocculation process. Also, all charge levels of the high molecular weight starches took longer to reach equilibrium flocculation than the medium and low molecular weight. For the reflocculation process, high-charged starches took less time than low-charged starches to achieve equilibrium state. Molecular weight affected flocculation, but not the reflocculation process. This suggests destruction of molecular weight by the high shear rates during the deflocculation step.

Table 18

The Time Required to Achieve Equilibrium Flocculation and Reflocculation of Nine Kinds of Cationic Starches Under 200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Charge level</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flocculation</td>
<td>Low</td>
<td>18</td>
<td>21</td>
<td>26</td>
<td>20</td>
<td>24</td>
<td>26</td>
<td>33</td>
<td>36</td>
<td>38</td>
</tr>
<tr>
<td>Reflocculation</td>
<td>Low</td>
<td>30</td>
<td>24</td>
<td>24</td>
<td>30</td>
<td>23</td>
<td>20</td>
<td>30</td>
<td>24</td>
<td>22</td>
</tr>
</tbody>
</table>

(Unit: sec)

*Figures for reflocculation are the averaged values of both 1100 and 2200 rpm.
The two way ANOVA based on the data of Table 18 are given in Table 19 and Table 20 for the flocculation and reflocculation, respectively. Table 19 shows both molecular weight and charge are significant effects at the 5% level of significance. Table 20 shows that only charge was significant at the 5% level of significance. This indicates that molecular weight has lost its effectiveness in affecting reflocculation. The low charge level starches for all three molecular weight levels took longer times to reflocculate than did the medium and high charge level starches.

Table 19

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>414.89</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>350.89</td>
<td>175.44</td>
<td>185.76</td>
<td>0.000</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>60.22</td>
<td>30.11</td>
<td>31.88</td>
<td>0.003</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>3.78</td>
<td>0.94</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>414.89</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Initial Rate of Flocculation

The average initial rate of flocculation is given in Table 21. The study of initial rate of flocculation was done by adding nine cationic starches, with three levels of charge and
Table 20

Least Squares ANOVA Molecular Weight and Charge Effects on the Time to Achieve Equilibrium Reflocculation Under 200 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>115.56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>4.22</td>
<td>2.11</td>
<td>1.90</td>
<td>0.263</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>106.89</td>
<td>53.44</td>
<td>48.10</td>
<td>0.002</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>4.44</td>
<td>1.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>115.56</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

molecular weight, under 200 rpm bob rotation. The two way ANOVA is given in Table 22. It can be seen that both charge and molecular weight significantly affected Rf at the 5% level of significance.

Table 21

The Average Initial Rate of Flocculation for Nine Kinds of Cationic Starches Under 200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Charge</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>High</td>
<td>3.00</td>
<td>2.78</td>
<td>5.78</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>0.98</td>
<td>1.65</td>
<td>3.08</td>
</tr>
<tr>
<td></td>
<td>Low</td>
<td>0.12</td>
<td>0.63</td>
<td>2.51</td>
</tr>
</tbody>
</table>

(Unit: mA/sec)
Table 22

Least Squares ANOVA Molecular Weight and Charge
Effects on Initial Rate of Flocculation
Under 200 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>23.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>12.13</td>
<td>6.07</td>
<td>36.64</td>
<td>0.003</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>10.40</td>
<td>5.20</td>
<td>31.41</td>
<td>0.004</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>0.66</td>
<td>0.17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>23.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

To further study the difference of charge and molecular weight, a 5% protected LSD analysis was performed. The results show that the decreasing trend of charge and molecular weight affecting Rf are:

$HMW > MMW = LMW$ and $HC > MC = LC$

Table 21 also shows that if charge was high, then excellent initial rate of flocculation occurred, regardless of molecular weight level. However, if charge was medium or low, only high molecular weights gave good rates of flocculation.

Initial Rate of Deflocculation

The average initial rate of deflocculation of four replicate runs is given in Table 23. The initial rate of deflocculation was studied by a three way ANOVA with charge, molecular weight, and shear, given in the Table 24. It shows that
molecular weight was the only significant main effect at the 5% level of significance, and interaction effects were not significant at the 25% level of the significance. Thus, the rate of deflocculation increased significantly as the molecular weight of the starch increased, whereas the level of charge on the starch had no significant effect. The two levels of shear used also gave no significant differences in rate of deflocculation.

Table 23
The Average Initial Rate of Deflocculation
For Nine Kinds of Cationic Starches
Under 1100 and 2200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Charge level</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>Low</td>
<td>.59</td>
<td>.81</td>
<td>.85</td>
</tr>
<tr>
<td>Charge level</td>
<td>Medium</td>
<td>.63</td>
<td>.72</td>
<td>-.1</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>-1.3</td>
<td>-2.9</td>
<td>-1.5</td>
</tr>
<tr>
<td>Shear</td>
<td>Low</td>
<td>.29</td>
<td>.51</td>
<td>.69</td>
</tr>
<tr>
<td></td>
<td>Medium</td>
<td>.62</td>
<td>.57</td>
<td>-.9</td>
</tr>
<tr>
<td></td>
<td>High</td>
<td>-.9</td>
<td>-.9</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

(Units: mA/sec)

Tables 25 and 26 were used to further study the influence of charge and molecular weight effects on the Rd. Table 25 (2200 rpm) shows that molecular weight effect and charge effect were not significant at the 5% level of significance. Table 26 (1100 rpm) showed that the both charge and molecular weight were significant effects for the Rd. Thus, charge and molecular weight were important in resisting shear at lower (1100 rpm) shear rate, but were not significant at the higher (2200 rpm) shear rate.
This suggests that the destruction of molecular weight might occurred under 2200 rpm.

### Table 24

**Analysis of Variance:**

Molecular Weight, Charge, and Shear Effects on the Initial Rate of Deflocculation (Rd)

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subclasses</td>
<td>5.80</td>
<td>17</td>
<td>0.34</td>
<td>2.077</td>
<td>0.251</td>
</tr>
<tr>
<td>A</td>
<td>0.61</td>
<td>1</td>
<td>0.61</td>
<td>3.727</td>
<td>0.126</td>
</tr>
<tr>
<td>B</td>
<td>2.68</td>
<td>2</td>
<td>1.34</td>
<td>8.149</td>
<td>0.039</td>
</tr>
<tr>
<td>C</td>
<td>0.51</td>
<td>2</td>
<td>0.26</td>
<td>1.560</td>
<td>0.316</td>
</tr>
<tr>
<td>AB</td>
<td>0.45</td>
<td>2</td>
<td>0.22</td>
<td>1.364</td>
<td>0.353</td>
</tr>
<tr>
<td>AC</td>
<td>0.48</td>
<td>2</td>
<td>0.24</td>
<td>1.450</td>
<td>0.336</td>
</tr>
<tr>
<td>BC</td>
<td>0.42</td>
<td>4</td>
<td>0.10</td>
<td>0.637</td>
<td>0.664</td>
</tr>
<tr>
<td>ABC</td>
<td>0.66</td>
<td>4</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(A: shear; B: molecular weight; C: charge)

### Table 25

**Least Squares ANOVA** Molecular Weight and Charge Effects on Initial Rate of Deflocculation (Rd) Under 2200 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>4.20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>2.57</td>
<td>1.29</td>
<td>5.03</td>
<td>0.081</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>0.61</td>
<td>0.31</td>
<td>1.20</td>
<td>0.391</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>1.02</td>
<td>0.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>4.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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Table 26

Least Squares ANOVA Molecular Weight and Charge Effects on Initial Rate of Deflocculation (Rd) Under 1100 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>0.56</td>
<td>0.28</td>
<td>20.81</td>
<td>0.008</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>0.38</td>
<td>0.19</td>
<td>14.14</td>
<td>0.015</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>0.05</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As mentioned above, since some deflocculation curves did not fit the quadratic model. An additional study of the second rate of deflocculation (Rd') at 0.5 second was required to provide more information about the deflocculation phenomena.

From the Table 27, it can be seen that only molecular weight of starch significantly affected Rd' at the 5% level of significance. The other effects were all non-significant at 5% or 25%.

From the studies of Rd, it can be concluded that the molecular weight effect and charge effect were significant at the beginning of the floc breakdown only under lower level shear (1100 rpm). The studies of Rd' showed that molecular weight was the only significant effects under both 1100 and 2200 rpm.
Table 27
Analysis of Variance Molecular Weight, Charge, and Shear Effects on Second Rate of Deflocculation (Rd') at 1100 and 2200 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of Squares</th>
<th>DF</th>
<th>Mean Square</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subclasses</td>
<td>1.86</td>
<td>17</td>
<td>0.11</td>
<td>3.080</td>
<td>0.142</td>
</tr>
<tr>
<td>A</td>
<td>0.22</td>
<td>1</td>
<td>0.22</td>
<td>6.311</td>
<td>0.066</td>
</tr>
<tr>
<td>B</td>
<td>0.98</td>
<td>2</td>
<td>0.49</td>
<td>13.733</td>
<td>0.016</td>
</tr>
<tr>
<td>C</td>
<td>0.13</td>
<td>2</td>
<td>0.06</td>
<td>1.763</td>
<td>0.283</td>
</tr>
<tr>
<td>AB</td>
<td>0.08</td>
<td>2</td>
<td>0.04</td>
<td>1.177</td>
<td>0.396</td>
</tr>
<tr>
<td>AC</td>
<td>0.15</td>
<td>2</td>
<td>0.07</td>
<td>2.047</td>
<td>0.244</td>
</tr>
<tr>
<td>BC</td>
<td>0.16</td>
<td>4</td>
<td>0.04</td>
<td>1.154</td>
<td>0.446</td>
</tr>
<tr>
<td>ABC</td>
<td>0.14</td>
<td>4</td>
<td>0.04</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(A: shear; B: molecular weight; C: charge)

Initial Rate of Reflocculation

The average initial rate of reflocculation is given in Table 28. The initial rate of reflocculation was studied during 200rpm bob rotation. Two two-way ANOVA, Tables 29 and 30, were used to study the influence of charge and molecular weight effects on the Rr.

The results showed that only charge significantly affected Rr at the 5% level of significance (following 2200 rpm). The other effects were all nonsignificant at the 5% level. It should be mentioned that Rf and Rr were measured at the same conditions and both charge and molecular weight were significant effects for
The reason for insignificant molecular weight effect on Rr is that molecular weight was probably reduced under high shear. Consequently, the only significant effect resulted from the charge.

Table 28

The Average Initial Rate of Reflocculation for Nine Kinds of Cationic Starches Following 1100 and 2200 rpm

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>Low</th>
<th>Medium</th>
<th>High</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge level</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low Shear 2200 rpm</td>
<td>0.6</td>
<td>1.0</td>
<td>2.2</td>
</tr>
<tr>
<td>Medium Shear 2200 rpm</td>
<td>0.8</td>
<td>1.5</td>
<td>2.2</td>
</tr>
<tr>
<td>High Shear 2200 rpm</td>
<td>1.8</td>
<td>1.9</td>
<td>2.1</td>
</tr>
<tr>
<td>Low Shear 1100 rpm</td>
<td>0.9</td>
<td>0.6</td>
<td>1.5</td>
</tr>
<tr>
<td>Medium Shear 1100 rpm</td>
<td>0.6</td>
<td>1.3</td>
<td>2.0</td>
</tr>
<tr>
<td>High Shear 1100 rpm</td>
<td>1.3</td>
<td>2.0</td>
<td>1.5</td>
</tr>
</tbody>
</table>

(Unit: mA/sec)

Table 29

Least Squares ANOVA Molecular Weight and Charge Effects on Initial Rate of Reflocculation Following 1100 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>2.07</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>2</td>
<td>0.52</td>
<td>0.26</td>
<td>1.30</td>
<td>0.367</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>0.75</td>
<td>0.37</td>
<td>1.87</td>
<td>0.267</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>0.80</td>
<td>0.20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>2.07</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 30
Least Squares ANOVA Molecular Weight and Charge Effects on Initial Rate of Reflocculation Following 2200 rpm

<table>
<thead>
<tr>
<th>Source</th>
<th>DF</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>PROB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cells</td>
<td>8</td>
<td>3.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>2</td>
<td>0.67</td>
<td>0.34</td>
<td>2.13</td>
<td>0.234</td>
</tr>
<tr>
<td>Charge</td>
<td>2</td>
<td>1.93</td>
<td>0.97</td>
<td>6.11</td>
<td>0.061</td>
</tr>
<tr>
<td>Charge-Molecular Wt.</td>
<td>4</td>
<td>0.63</td>
<td>0.16</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>8</td>
<td>3.24</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The possible explanation for the insignificant charge and molecular weight effects following 1100 rpm is that the molecular weight effect might not be totally destroyed by the shear. Thus, reflocculation might be due to either charge or molecular weight effects. On the other hand, molecular weight might be destroyed during 2200 rpm and results in charge being the only significant effect.
CHAPTER VI

SUMMARY OF RESULTS

A series of cationic starches with three levels of charge and molecular weight were used to investigate the role of starch charge and starch molecular weight in a system of fines and clay under dynamic shear. The experimental data have been analyzed from various angles in the previous chapter. The summary of statistical results is listed in Table 31, where the main effects were tested at 5% level of significance, and the interaction terms were tested at 25% level of significance. Further analyses of the main effects were made by using the 5% protected LSD test.

In the flocculation process, it was found that both charge and molecular weight were significant effects for the amount of flocculation (H1) and the rate of flocculation (Rf). The ability to increase flocculation was associated with increasing charge and molecular weight of the starch. However, this trend was unable to explain the similar flocculation generated by starches with different charges and molecular weight, where interaction effects play an important role. Consequently, both main and interaction effects were significant for developing flocculation of fines and filler clay.

The H2, t2, Rd, and Rd' were used for investigating the phenomena of deflocculation. It was obvious that charge, shear,
Table 31

Summary Results of Two-way and Three-way ANOVA
(Main effects were tested at 5%, and interaction effects were tested at 25% level of significance)

<table>
<thead>
<tr>
<th></th>
<th>a H1</th>
<th>H2</th>
<th>H3</th>
<th>H3/H1 t2</th>
<th>Rf</th>
<th>Rd</th>
<th>Rd'</th>
<th>Rr</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Main Effects:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molecular weight</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>NS*</td>
<td>S</td>
<td>NS</td>
</tr>
<tr>
<td>Charge</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>NS*</td>
<td>NS</td>
<td>S**</td>
</tr>
<tr>
<td>Shear</td>
<td>-***</td>
<td>S</td>
<td>S</td>
<td>NS</td>
<td>S</td>
<td>-</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td><strong>Interaction Effects:</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shear-Molecular wt.</td>
<td>-</td>
<td>S</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
<td>-</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Shear-Charge</td>
<td>-</td>
<td>S</td>
<td>S</td>
<td>NS</td>
<td>NS</td>
<td>-</td>
<td>NS</td>
<td>NS</td>
</tr>
<tr>
<td>Molecular wt-Charge</td>
<td>S</td>
<td>NS</td>
<td>S</td>
<td>S</td>
<td>NS</td>
<td>-</td>
<td>NS</td>
<td>-</td>
</tr>
</tbody>
</table>

* With isolation of shear effects,charge and molecular weight were the significant effects under 1100 rpm.
** Charge was a significant effect following 2200 rpm deflocculation curves.
*** Two way ANOVA were used. Both main and interaction effects of shear were not under investigation.

a Terms defined on p. 32 and 33

and molecular weight were all significant effects for the amount of flocs retained after high shear (H2) and the time to achieve total deflocculation (t2). The study of t2 revealed that the high-shear-resistant flocs generally were formed by either high charge (HC) or high molecular weight (HMW) starch. However, under the lower level of high shear (1100 rpm), the strength of flocs was dependent on the differences of charge instead of the differences of molecular weight. The study of H2 revealed that some flocs still could be retained after the high shear process. The relative-particle-size concept was used to interpret this phenomena.
Molecular weight and charge were significant effects for the time required to achieve equilibrium flocculation. Charge was the only significant effect for the time required to achieve equilibrium reflocculation.

The analysis of initial rate of deflocculation (Rd) revealed that molecular weight and charge were the significant effects for Rd only under lower level shear (1100 rpm). From the study of second rate of deflocculation (Rd'), molecular weight was the only significant effect under 1100 and 2200 rpm. From the study of deflocculation curves, it was learned that the initial linear behavior associated with the starches represented high-shear-resistant flocs. This is possibly due to the compression and shielding effects. Figure 13 was used to interpret this phenomenon.

The amount of reflocculation (H3) and the initial rate of reflocculation (Rr) were used to study the phenomena of reflocculation. The results showed that charge, shear, and molecular weight were significant effects for H3. Generally, the HC or HMW starch resulted in a high extent of reflocculation. Studies of the interaction terms reveal that interaction effects, such as charge and molecular weight also played an important role in developing H3. Consequently, both main and interaction effects played important roles in promoting reflocculation. From the analysis of Rr, charge was the only significant effect following 2200 rpm. The molecular weight effect, in this case, was insignificant for Rr. This could be explained by the
likelihood that reduction of molecular weight occurred under high shear.

The study of the amount of flocs recovered after removing the high shears (H3/H1) revealed, except for IMW-LC and MMW-LC, more than 50% flocs could be recovered.
CHAPTER VII

CONCLUSIONS

From the experimental data obtained in this study, the following conclusions can be drawn:

1. Charge and molecular weight were significant effects for the amount of flocculation (H1), the amount of flocs retained after high shear (H2), the initial rate of flocculation (Rf) and the total time to achieve equilibrium state (t2). For the initial rate of deflocculation (Rr), charge was the only significant effect following 2200 rpm deflocculation. For the initial rate of deflocculation (Rd), the molecular weight and charge were the significant effects under 1100 rpm. For the second rate of deflocculation (Rd'), molecular weight was the only significant effect under both 1100 and 2200 rpm.

2. Molecular weight and charge were significant effects for the time required to achieve equilibrium flocculation. Charge was the significant effect for the time required to achieve equilibrium reflocculation.

3. Interaction effects between charge and molecular weight were found to play an important role in determining flocculation. In another words, similar flocculation behavior was promoted by starches with different combinations of charge and molecular weight.
4. The reduction of molecular weight of starches under high shear was suggested by the study of the amount of flocs recovered following high shear.

5. The linear behavior of the deflocculation curves was associated with starches which could promote high-shear-resistant flocs. The compression and shielding effects were used to interpret this phenomenon. Nevertheless, further proof is needed for this interpretation.

6. The high shear used in this study was unable to totally break up the flocs in some cases. This gave evidence for the relative-particle-size concept, where the flocs formed by two unequal-sized particles with high molecular weight polymer conceivably presented high tolerance to shear.

7. The study of percent floc recovery showed that no flocs can be totally recovered after high shears, this suggested that the possible mechanism in this study was bridging. However, more study is needed to verify this statement.
CHAPTER VIII

SUGGESTIONS FOR FURTHER STUDY

Further experimental research and modification of the instrument are recommended in the following areas:

1. Molecular weight studies should be conducted after high shear application at different elapsed times to verify the concept of compression and shielding effects. Zeta potential measurements could be used to confirm the assumptions concerning the flocculation mechanism involved.

2. Instrument improvements should be made by adding an automatic timing loop to control rotation speed of bob. This would enhance the accuracy of control, and also make possible experiments performed within a few seconds.

3. The time consuming procedure of curve fitting could be avoided by connecting a microcomputer with graphic function ability to the output of the instrument.

4. The study should be repeated with polymers which contain a broader range of charge and molecular weight. The different flocculation mechanisms might be verified by this approach.

5. A simpler particle geometry colloid system such as monodispersed latex particles could be used to facilitate interpretation of phenomena.
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Appendix A

Calculations of the Shear Apparatus
Appendix A

Calculations of the Shear Apparatus

The following calculations are based on the equations listed on page 29 and 31.

Shear rate at 200 rpm bob rotation:

\[
\dot{\gamma} = \frac{2 (200 \times 6.2827/60) (1.925/1.7)^2}{(1.925/1.7) - 1} - 1 = 190 \text{ sec}
\]

Shear rate at 1100 rpm bob rotation:

\[
\dot{\gamma} = \frac{2 (1100 \times 6.2827/60) (1.925/1.7)^2}{(1.925/1.7) - 1} = 1045 \text{ sec}
\]

Shear rate at 2200 rpm bob rotation:

\[
\dot{\gamma} = \frac{2 (200 \times 6.2827/60) (1.925/1.7)^2}{(1.925/1.7) - 1} = 2090 \text{ sec}
\]

Transition rpm and shear rate in the system:

\[
p = 0.0571 \left[1 - 0.062(0.225)/1.7\right]^{-1} + 0.00056 \left[1 - 0.658(0.225)/1.7\right]^{-1} = 0.05724
\]

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\[
0.05724 = \frac{353.1}{2 Q (0.225)^2 (1.925)^2}, \text{ thus } Q = 270.3
\]

Transition rpm = \(270.3 \times 60 / 6.2827 = 2580 \text{ rpm}\)

Transition \(r = \frac{2 (270.3) (1.925/1.7)^2}{(1.925/1.7) - 1} = 2456 \text{ sec}\)
Appendix B

Preparation of Fines and Clay Suspension
Appendix B

Preparation of Fines and Clay Suspension

1. 320g Weyerhaeuser bleached hardwood was beaten in a Valley beater to CSF Freeness of 300 ml.

2. The fines suspension was collected by using a Britt jar with 200 mesh (75 micron screen).

3. Repeated procedure 1 and 2 until 60 liters fines of suspension was collected.

4. Stored fines suspension in four plastic containers for at least 12 hours. Then carefully removed upper clear filtrate and replaced with distilled water.

5. Repeated above procedure four times to increase the concentration of fines and to reduce the hardness of the water.

6. 100 ml final of fines suspension was filtered on a preweighed filter paper to determine the solids content. 0.08% fines suspension was obtained and used in this study.

7. Filler clay was added to the fines suspension to obtain 50% loading of filler based on fines. The final filler/fines suspension was 0.12% total solids and contained 0.08% fines and 0.04% filler by weight.

8. Finally, 0.1N H SO4 was used to adjust the pH of the suspension to 4.5.
Appendix C

Cationic Starch Preparation
Appendix C

Cationic Starch Preparation

A series of cationic starches were prepared by Richard Harvey of the Grain Processing Corporation, using waxy maize as the base starch. The following table describes the starches:

<table>
<thead>
<tr>
<th>Molecular weight</th>
<th>High</th>
<th>Medium</th>
<th>Low</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Ammonium Persulfate:</td>
<td>0.0000</td>
<td>0.2500</td>
<td>0.1000</td>
</tr>
<tr>
<td>Degree of Substitution:</td>
<td>0.0140</td>
<td>0.0130</td>
<td>0.0136</td>
</tr>
<tr>
<td></td>
<td>0.0226</td>
<td>0.0247</td>
<td>0.0220</td>
</tr>
<tr>
<td></td>
<td>0.0307</td>
<td>0.0328</td>
<td>0.0325</td>
</tr>
<tr>
<td></td>
<td>0.0833</td>
<td>0.0883</td>
<td>0.0852</td>
</tr>
<tr>
<td></td>
<td>0.1494</td>
<td>0.1550</td>
<td>0.1397</td>
</tr>
</tbody>
</table>

Those starches were precipitated from the paste form in which they were converted using methanol. The degree of substitution data, obtained from Kjeldahl procedure for nitrogen determination, was provided by the starch supplier. Since it was difficult to totally dissolve the high D.S. (0.1400) starch, only nine starches were used in the study (refer to page 38).

The procedure to prepare the working solution was as follows:

1. 0.5g of cationic starch was placed in a one liter beaker with 800 ml distilled water.
2. The starch dispersion was heated to 195°F for 40 minutes.
   Gentle agitation was applied by a three-blade stirrer.
3. Final solution was stored in a sealed bottle to prevent contamination.
Appendix D

Simulation of the Flocculation, Deflocculation, and Reflocculation Curves
Appendix D

Simulation of the Flocculation, Deflocculation, and Reflocculation Curves

The mathematical equations for flocculation, deflocculation, and reflocculation curves are listed below. Since two levels of high shear were used in each experiment, there were 5 equations for each starch: one for flocculation, two for deflocculation, and two for reflocculation. In the cases of linear behavior of deflocculation curves, two equations were used to simulate each deflocculation curve. Methods used to obtain these equations have been discussed in the body of this paper.
HMW-HC cationic starch:

\[ A: \quad Y = -0.352X + 5.78X + 2.445 \]
\[ B: \quad Y = -0.104X + 2.062X + 0.168 \]
\[ C: \quad Y = -0.126X + 1.97X + 0.503 \]
\[ D: \quad Y = -0.028X -1.11X - 0.441 ; Y = -1.0X \]
\[ E: \quad Y = 0.034X - 1.334X - 0.318 ; Y = -1.0X \]

HMW-MC cationic starch:

\[ A: \quad Y = -0.129X + 3.077X + 0.225 \]
\[ B: \quad Y = -0.11X + 1.919X + 0.645 \]
\[ C: \quad Y = -0.91X + 1.5X + 0.607 \]
\[ D: \quad Y = 0.002X - 1.209X - 0.295 \]
\[ E: \quad Y = 0.007X - 0.515X - 0.298 \]

HMW-LC cationic starch:

\[ A: \quad Y = -0.106X + 2.506X + 0.145 \]
\[ B: \quad Y = -0.112X + 1.796X + 0.941 \]
\[ C: \quad Y = -0.073X + 1.266X + 0.536 \]
\[ D: \quad Y = 0.047X - 1.517X - 0.223 \]
\[ E: \quad Y = 0.025X - 0.867X - 0.35 \]
MMW-HC cationic starch:

\[
\begin{align*}
A: & \quad Y = -0.08X + 2.783X + 0.355 \\
B: & \quad Y = -0.13X + 2.238X + 0.568 \\
C: & \quad Y = -0.127X + 1.945X + 0.513 \\
D: & \quad Y = -0.002X - 0.493X - 0.238 ; Y = -1.3X \\
E: & \quad Y = -0.017X - 0.504X - 0.208 ; Y = -0.7X \\
\end{align*}
\]

MMW-MC cationic starch:

\[
\begin{align*}
A: & \quad Y = -0.07X + 1.65X + 0.2 \\
B: & \quad Y = -0.07X + 1.47X + 0.268 \\
C: & \quad Y = -0.042X + 1.248X + 0.095 \\
D: & \quad Y = 0.005X - 0.716X - 0.24 ; Y = -2.9X \\
E: & \quad Y = 0.013X - 0.57X + 0.26 ; Y = -0.9X \\
\end{align*}
\]

MMW-LC cationic starch:

\[
\begin{align*}
A: & \quad Y = -0.025X + 0.625X - 0.005 \\
B: & \quad Y = -0.042X + 0.825X + 0.287 \\
C: & \quad Y = -0.026X + 0.602X + 0.086 \\
D: & \quad Y = 0.02X - 0.634X - 0.319 ; Y = -1.5X \\
E: & \quad Y = 0.031X - 0.627X - 0.243 ; Y = -1.5X \\
\end{align*}
\]
LMW-HC cationic starch:

A: \( Y = -0.127X + 3.0X - 0.14 \)

B: \( Y = -0.042X + 0.825X + 0.287 \)

C: \( Y = -0.09X + 1.46X + 0.627 \)

D: \( Y = -0.016X - 0.848X - 0.042 ; Y = -2.1X \)

E: \( Y = 0.007X - 0.694X - 0.195 ; Y = -1.2X \)

LMW-MC cationic starch:

A: \( Y = -0.012X + 0.98X + 0.353 \)

B: \( Y = -0.05X + 1.167X + 0.264 \)

C: \( Y = -0.053X + 1.007X + 0.3 \)

D: \( Y = 0.028X - 0.591X + 0.208 \)

E: \( Y = -0.008X - 0.294X - 0.354 \)

LMW-LC cationic starch:

A: \( Y = -0.003X + 0.12X + 0.093 \)

B: \( Y = -0.038X + 0.55X + 0.33 \)

C: \( Y = -0.044X + 0.916X + 0.1 \)

D: \( Y = 0.013X - 0.81X - 0.8 \)

E: \( Y = 0.009X - 0.506X - 0.19 \)
Appendix E

Various Shear Rates of The Wet End System
Appendix E

Various Shear Rates of The Wet End System

According to d’Incan estimations (42), the rates of shear existing in various locations of a paper machine operating at 15 m/s (2700 ft/min) were as follows:

<table>
<thead>
<tr>
<th>Elements</th>
<th>Mean shear rate, 1/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Headbox:</td>
<td>2</td>
</tr>
<tr>
<td>Parallel section</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Turbulence generator</td>
<td>10 - 10</td>
</tr>
<tr>
<td>Slice</td>
<td>10</td>
</tr>
<tr>
<td>Pipe</td>
<td>10</td>
</tr>
<tr>
<td>Table roll</td>
<td>10</td>
</tr>
<tr>
<td>Foil</td>
<td>10</td>
</tr>
</tbody>
</table>

In this study, the shear rate used in the zone I and III was 190 1/s, which is close to that of pipe, foil, and table roll. The shear rates used in the zone II was 1045 and 2090 1/s, which are in the range of shear rate of the headbox.
Appendix F

Program for Data Management
Appendix F

Program for Data Management

program thesis;

type
  intype = array [1..120] of integer;
  retype = array [1..120] of real;
  twotype = array [1..50,1..121] of real;
  chartype = array [1..15] of char;
var
  xresult, yresult: retype;
  answer: chartype;
  y: twotype;
  count, t, x: integer;

procedure readdata(var f: chartype);

var
  i: integer;
  ch: char;
begin
  for i := 1 to 15 do
    f[i] := ' ';
  read(kbd,ch); i := 0;
  while (ch <> #13) do
    begin
      if ch in ['0'..'9','.','','-'] then
        begin
          i := i + 1; f[i] := ch;
        end
      else
        begin
          write(trm,'Sorry! you typed the wrong ');
          writeln(trm,'number, please try again. ');
          i := 0;
        end;
    read(kbd,ch);
  end; (* of readdata *)
(* function convert *)

function convert: real;

var
  i, j, k: integer;
  val, val1, val2, n: real;
  negative, found: boolean
begin
  negative := false;  found := false;  j := 0;
  val1 := 0.0;  val2 := 0.0;  val := 0.0;
  if answer[1] = '-' then
    begin (* check the negative real number *)
      i := 2;  negative := true
    end
  else i := 1;
  while (i <= 15) and (answer[i] <> '') do
    begin
      if (answer[i] <> '.') and (not found) then
        begin (* integer number *)
          val1 := val1 * 10.0 + ord(answer[i]) - 48.0;
        end
      else
        begin (* real number *)
          if answer[i] = '.' then
            i := i + 1;
          val2 := (ord(answer[i])) - 48.0;
          j := j + 1;  found := true;
          for k := 1 to j do
            val2 := val2 / 10.0;
          val := val + val2
        end;
      i := i + 1;
    end;
  if negative then
    convert := 0 - (val1 + val)
  else convert := val1 + val;
end;

(* procedure readmenu *)

procedure readmenu(var a, b, c: integer);
```pascal
var
  i : integer;
begin
  for i := 1 to 3 do
    case i of
    1 : begin
      ClrScr;
      write(trm,'Please enter the number of');
      writeln(trm,' experiments');
      readdata(answer);
      a := trunc(convert); writeln(trm,a)
    end;
    2 : begin
      write(trm,'Please enter the maximum ');
      writeln(trm,'time of experiments ');
      readdata(answer);
      b := trunc(convert); writeln(trm,b);
    end;
    3 : begin
      write(trm,'please enter the measurement');
      writeln(trm,' of each experiment');
      readdata(answer);
      c := trunc(convert); writeln(trm,c);
    end;
    end; (* of case *)
end; (* of readmenu *)
```

```
procedure ydatain(c,n: integer; var f: twotype);
var
  i,j : integer;
begin
  for i := 1 to c do
    begin
      ClrScr;
      writeln(trm,'please enter ',i,' experiment of ');
      for j := 1 to n + 1 do
        begin
          writeln(trm,'y',j-1); readdata(answer);
          f[i,j] := convert; writeln(trm,f[i,j])
        end;
    end;
end; (* of ydatain *)
```
(* procedure compute *)
(procedure compute(t: twotype; n, n1, n2: integer);
    var
        temp : real;
        i, j : integer;
    begin
        xresult[1] := 0.0;
        for i := 2 to n1+1 do
            xresult[i] := xresult[i-1] + n/n1;
        for i := 1 to n1+1 do
            begin
                temp := 0.0;
                for j := 1 to n2 do
                    temp := temp + t[j, i];
                yresult[i] := temp/n2;
            end;
    end; (* of compute *)
(* procedure writeout *)
(procedure writeout(x: integer);
    const
        blank = ' ';
    var
        ch : char;
        i, j : integer;
    begin
        ClrScr; j := 0; writeln(trm); writeln(trm);
        writeln(trm, blank:12, 'X', blank:14, 'Y');
        for i := 1 to x+1 do
            begin
                j := j + 1;
                if j = 20 then
                    begin
                        j := 0;
                        repeat
                            write(trm, 'Please hit the return to rece');
                            writeln(trm, 'Ive more data'); read(kbd, ch);
                            until ch = #13;
                        ClrScr; writeln(trm); writeln(trm);
                    end;
                    writeln(trm, xresult[i]:15:2, yresult[i]:15:2);
            end;
    end; (* of writeout *)
)
(*******************************************************************************)
(* main program *)
(*******************************************************************************)

begin
    Textcolor(1);
    TextBackground(7);
    readmenu(count,t,x);
    ydatain(count,x,y);
    compute(y,t,x,count);
    writeout(x);
end.
Appendix G

Summary of Experimental Curves
Appendix G

Summary of Experimental Curves

According to the results obtained from Appendix D, a series of figures (a to i) can be drawn for the nine kinds of cationic starches. It should be mentioned that all the drawings are based on mathematical calculations rather than the direct output of the instrument. In another words, each curve is a "mean" of four runs.

A preliminary test by adding water to the cup and bob assembly read 8.4 mA. This figure was used as a basis for converting all the test results (mA) to relative turbidity units. For example, the amount of flocculation (H1) for HMW-LC cationic starch was 3.9 mA. The relative turbidity then can be calculated by the equation listed below:

\[
\text{Relative Turbidity (\( \tau \))} = - \ln \frac{3.9 \text{ mA}}{8.4 \text{ mA}} = 0.77
\]

It should be mentioned that the reading from the original sample which contain fines/clay suspension was 5.0 mA in this study. This figure was used as "zero" basis throughout this study. For example, H2 for HMW-HC under 1100 rpm in Table 7 was 0.4 mA which was read based on the original sample. The actual reading should be 4.6mA in this case (5.0 - 0.4 = 4.6). On the other hand, the H2 for MMW-LC under 1100 rpm in Table 7 was -0.2 mA. The actual reading should be 5.2 mA (5.0 + 0.2 =5.2).
(a) Flocculation, deflocculation, and reflocculation curves for \( M \) cationic starch.
(b) Flocculation, deflocculation, and reflocculation curves for IM-K+ cationic starch
(d) Flocculation, deflocculation, and reflocculation curves for IMC catonic starch.
Flocculation, deflocculation, and reflocculation curves for kaolin starch

(e) Flocculation, deflocculation, and re-flocculation curves for kaolin starch

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(f) Flocculation, deflocculation, and reflocculation curves for MM-80 native potato starch.
(h) Flocculation, deflocculation, and reflocculation curves for DMA-HE cationic starch
Summary of Test Results

### Amount of Flocculation (H1)

<table>
<thead>
<tr>
<th>Cationic Starch</th>
<th>Data</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMW-HC</td>
<td>34.8 35.1 35.2 34.9</td>
<td>35.0</td>
<td>0.18</td>
</tr>
<tr>
<td>HMW-MC</td>
<td>24.9 24.7 25.2 25.1</td>
<td>25.0</td>
<td>0.22</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>21.7 21.9 22.3 22.2</td>
<td>22.0</td>
<td>0.27</td>
</tr>
<tr>
<td>MMW-HC</td>
<td>23.7 24.0 23.9 24.4</td>
<td>24.0</td>
<td>0.29</td>
</tr>
<tr>
<td>MMW-MC</td>
<td>13.1 12.8 13.0 13.1</td>
<td>13.0</td>
<td>0.14</td>
</tr>
<tr>
<td>MMW-LC</td>
<td>8.8 9.2 8.8 9.1</td>
<td>9.0</td>
<td>0.21</td>
</tr>
<tr>
<td>LMW-HC</td>
<td>20.3 20.4 20.8 20.5</td>
<td>20.5</td>
<td>0.22</td>
</tr>
<tr>
<td>LMW-MC</td>
<td>5.0 4.9 5.0 5.0</td>
<td>5.0</td>
<td>0.05</td>
</tr>
<tr>
<td>LMW-LC</td>
<td>2.4 2.4 2.5 2.7</td>
<td>2.5</td>
<td>0.14</td>
</tr>
</tbody>
</table>

(Unit: x0.05mA)

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Amount of Reflocculation Following 1100 and 2200 rpm (H3)

<table>
<thead>
<tr>
<th>Cationic Starch</th>
<th>1100 rpm</th>
<th>2200rpm</th>
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<tbody>
<tr>
<td></td>
<td>Data</td>
<td>Mean</td>
</tr>
<tr>
<td>HMW-HC</td>
<td>21.4 21.7 21.5 21.6</td>
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</tr>
<tr>
<td>HMW-MC</td>
<td>13.4 13.5 13.5 13.6</td>
<td>13.5</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>13.9 14.1 14.0 14.1</td>
<td>14.0</td>
</tr>
<tr>
<td>MMW-HC</td>
<td>12.8 13.1 13.0 12.9</td>
<td>13.0</td>
</tr>
<tr>
<td>MMW-MC</td>
<td>6.4 6.5 6.4 6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>MMW-LC</td>
<td>1.4 1.6 1.5 1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>LMW-HC</td>
<td>11.8 11.7 12.1 12.2</td>
<td>12.0</td>
</tr>
<tr>
<td>LMW-MC</td>
<td>6.0 6.1 5.9 6.0</td>
<td>6.0</td>
</tr>
<tr>
<td>LMW-LC</td>
<td>0.9 0.9 1.0 1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>HMW-HC</td>
<td>20.4 20.3 20.6 20.5</td>
<td>20.5</td>
</tr>
<tr>
<td>HMW-MC</td>
<td>12.9 13.1 13.2 13.0</td>
<td>13.0</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>12.5 12.6 12.5 12.5</td>
<td>12.5</td>
</tr>
<tr>
<td>MMW-HC</td>
<td>11.8 12.1 12.0 11.9</td>
<td>12.0</td>
</tr>
<tr>
<td>MMW-MC</td>
<td>6.3 6.5 6.4 6.5</td>
<td>6.5</td>
</tr>
<tr>
<td>MMW-LC</td>
<td>1.5 1.4 1.5 1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>LMW-HC</td>
<td>10.8 11.2 11.0 11.1</td>
<td>11.0</td>
</tr>
<tr>
<td>LMW-MC</td>
<td>5.9 6.1 6.0 5.8</td>
<td>6.0</td>
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<tr>
<td>LMW-LC</td>
<td>0.9 1.1 1.0 1.0</td>
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(Unit: x0.05mA)

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Amount of Flocs Retained Under 1100 and 2200 rpm (H2)

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<th>Data</th>
<th>Mean</th>
<th>S.D.</th>
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</thead>
<tbody>
<tr>
<td>HMW-HC</td>
<td>7.8</td>
<td>8.0</td>
<td>0.17</td>
</tr>
<tr>
<td>HMW-MC</td>
<td>4.7</td>
<td>5.0</td>
<td>0.21</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>3.8</td>
<td>4.0</td>
<td>0.13</td>
</tr>
<tr>
<td>HMW-HC</td>
<td>2.8</td>
<td>3.0</td>
<td>0.21</td>
</tr>
<tr>
<td>HMW-MC</td>
<td>0.0</td>
<td>0.0</td>
<td>0.05</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>-4.9</td>
<td>-5.0</td>
<td>0.24</td>
</tr>
<tr>
<td>LMW-HC</td>
<td>1.7</td>
<td>2.0</td>
<td>0.27</td>
</tr>
<tr>
<td>LMW-MC</td>
<td>-0.9</td>
<td>-1.0</td>
<td>0.10</td>
</tr>
<tr>
<td>LMW-LC</td>
<td>-4.8</td>
<td>-5.0</td>
<td>0.17</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cationic Starch</th>
<th>Data</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMW-HC</td>
<td>2.9</td>
<td>3.0</td>
<td>0.06</td>
</tr>
<tr>
<td>HMW-MC</td>
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<td>0.0</td>
<td>0.10</td>
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<td>HMW-LC</td>
<td>0.0</td>
<td>0.0</td>
<td>0.08</td>
</tr>
<tr>
<td>LMW-HC</td>
<td>-0.1</td>
<td>0.0</td>
<td>0.10</td>
</tr>
<tr>
<td>LMW-MC</td>
<td>-2.9</td>
<td>-3.0</td>
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<tr>
<td>LMW-LC</td>
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<tr>
<td>LMW-HC</td>
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<td>LMW-MC</td>
<td>-3.5</td>
<td>-3.5</td>
<td>0.05</td>
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<tr>
<td>LMW-LC</td>
<td>-4.9</td>
<td>-5.1</td>
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</tr>
</tbody>
</table>

(Unit: x0.05mA, "+" and "-" mean above or below original sample)
The Time Required to Achieve Equilibrium Deflocculation under 1100 and 2200 rpm (t2)

<table>
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<tr>
<th>Cationic Starch</th>
<th>Data</th>
<th>Mean</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
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<td></td>
<td></td>
</tr>
<tr>
<td>HMW-HC</td>
<td>4.9</td>
<td>4.9</td>
<td>0.10</td>
</tr>
<tr>
<td>HMW-MC</td>
<td>4.4</td>
<td>4.2</td>
<td>0.21</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>3.0</td>
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<td>0.05</td>
</tr>
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<td>4.4</td>
<td>0.10</td>
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<tr>
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<td>2.6</td>
<td>0.13</td>
</tr>
<tr>
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<td>3.9</td>
<td>0.13</td>
</tr>
<tr>
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<td>2.4</td>
<td>0.10</td>
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<tr>
<td>LMW-LC</td>
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<td>0.06</td>
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<tr>
<td>2200 rpm</td>
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<td></td>
</tr>
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<td>4.5</td>
<td>0.13</td>
</tr>
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<td>HMW-MC</td>
<td>3.2</td>
<td>3.3</td>
<td>0.14</td>
</tr>
<tr>
<td>HMW-LC</td>
<td>2.1</td>
<td>2.3</td>
<td>0.13</td>
</tr>
<tr>
<td>HMW-HC</td>
<td>3.4</td>
<td>3.6</td>
<td>0.12</td>
</tr>
<tr>
<td>HMW-MC</td>
<td>2.2</td>
<td>2.2</td>
<td>0.17</td>
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<tr>
<td>HMW-LC</td>
<td>1.7</td>
<td>1.7</td>
<td>0.05</td>
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<tr>
<td>LMW-HC</td>
<td>3.1</td>
<td>3.0</td>
<td>0.13</td>
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<tr>
<td>LMW-LC</td>
<td>1.1</td>
<td>1.1</td>
<td>0.13</td>
</tr>
</tbody>
</table>

(Unit: sec)
Appendix I

Welch Pairwise Comparison Among Nine Kinds of Cationic Starches
Appendix I

Welch Pairwise Comparision Among Nine Kinds of Cationic Starches

According to Table 6, it can be seen that F probability values for groups 1-6, 1-9, 2-6, and 6-9 were greater than 0.05, which showed there were no significant differences between group-group. By using "underline" technique listed below. It can be concluded that group 9 (HMW-LC), 6 (HMW-MC), 2 (MMW-HC), and 1 (LMW-HC) had no significant differences in developing flocculation at the 5% level of significance.

Group: 1  2  6  9
      -  -  -  -
      -  -  -  -
      -  -  -  -

Conclusion: 1 = 2 = 6 = 9
BIBLIOGRAPHY


Waech, T. G. "Improving Filler Retention by Adding Filler After Retention Aid Addition," Tappi, 66(3): 137(1983)