A SINGLE FLOCCULANT/DUAL FLOCCULATION SYSTEM FOR DEWATERING USING A BRANCHED SELF INVERSING EMULSION FLOCCULANT

Young-Han Bae and Sung-Sik Lee[†]

Department of Chemical Engineering, Dong-A University 840 Hadan-2-Dong, Saha-Ku, 604-714, Busan, KOREA

Abstract : In order to create a single flocculant/dual flocculation system, polyacrylamide-co-trimethyl ammonium ethyl acrylate chloride (TAEAC) polymers with varying molecular weights and structures were prepared for use of flocculants. The higher the cationic density of the polymer is higher, the higher was the conversion rate and the ratio of monomer. An acrylamide as nonionic monomer was less reactive than a TAEAC as cationic monomer. The branched polymer which was polymerized with a cross-linking agent, N, N-methylene bis-acrylamide had a higher stability and higher viscosity than a linear polymer but its dewatering efficiency was poor in a single flocculation system. In the case of single flocculant/dual flocculation, the branched polymer has better flocculation efficiency and the water content of the dewatered cakes was lower than the others, as the result of a re-flocculation effect. The optimum conditions for dual flocculation are a sequence in which the 1st and 2nd dosage are 75% and 25%/total dosage of a single flocculation system. The dewatering efficiency of a dual flocculation system is improved considerably from 10 to 25% under the experimental conditions used herein.

Key Words : Polyacrylamide, Flocculation, Dewatering, Branched polymer, N,N-methylene bis-acrylamide

INTRODUCTION

A synthetic polyelectrolyte is a polymer derived from petrochemical-derived materials, carrying ionic charges along the polymer chains, causing the polymer to be water-soluble[1]. Polyacrylamides are high molecular weight, water-soluble polymers and are typically employed in solid/liquid separation processes. These materials induce flocculation by agglomerating solids and, hence, improving the rate of dewatering of many suspensions in the fields of municipal and industrial water treatment, in mining, metal recovery, and in paper making[2].

In recent years, the performance of these flocculants has been improved. One such improvement is "structuring" the linear products through the use of suitable cross-linking/branching agents. However, the normal flocculant is a powder type and the branched or cross-linked type polymers are more difficult to dissolve in water than linear type polymers. It only swells or absorbs with water. However, an emulsion has a superior solubility than a powder, because these formulations are capable of forming micelles. A general emulsion flocculant is a self-inversing emulsion by an inversing agent when it is dissolved[3-4].

Another type is a "flocculation system" comprised of various chemicals and reactions.

In many industrial processes, the use of combinations of oppositely charged polyelectrolytes under suitable conditions enhances flocculation. Although such combinations are increasingly used

[†] Corresponding author
E-mail: hanchemen@yahoo.co.kr
Tel: +82-(0)51-200-7721 , Fax: +82-(0)51-200-7728

as flocculants in industry, a limited amount of mechanistic or other research is currently available. Yu et al.[6] investigated the dual polymer flocculation of alumina particles and Petzold et al.[7] studied the effect of charge ratios of two oppositely charged polymers and the influence of polymer molecular weight on flocculation. Some researchers have estimated the combination between coagulant and flocculant and the mechanism of coagulation or flocculation[5-8].

In this study, we estimated the characteristics of structured polyacrylamide self-inversing emulsion with N, N-methylene bis-acrylamide (MBA) at various conditions.

The flocculation of sewage conditioning sludge with a single flocculant/dual flocculation, and with various modes of polymer additions, was investigated. The flocculation efficiency of the polymers, expressed in terms of drainage was measured along with the dosage, ionicity and the structure of the polymer.

Based on the results obtained, the optimization and mechanism of single flocculant/dual flocculation for improving dewatering efficiency was examined, using a slightly branched polymer.

MATERIAL AND METHODS

Emulsion Polymerization

Acrylamide (AAM) and trimethyl ammonium ethyl acrylate chloride (TMAEAC), as a cationic monomer were polymerized by a free radical initiated reactions in distilled water at 40~60°C. Potassium persulfate (Jun Sei, reagent grade) was used as the water soluble initiator. An isoparaffinic solvent from Exxon was used as the oil phase. Sorbitan monooleate (HLB=4.3), Sorbitan sesquioleate (HLB=3.7), POE (20) sorbitan monostearate (HLB=14.9) and polymeric emulsifier (HLB=6.0) were used as emulsifiers.

The polymerization was carried out in a 1 L round bottomed flask equipped with a mechanical stirrer, a nitrogen inlet/outlet and a digital thermometer[9].

After both the monomer phase and oil phase were prepared, the phases were emulsified using a homogenizer, generating an oil-in-water emulsion (O/W Emulsion).

Polymerization times were varied between 40 and 120 min, and the inversing time was 30 min. Various molecular weights polymers were produced by altering the concentrations of monomer and initiator, and occasionally adding very small amounts of ethylene bis-acrylamide as a cross linking agent[10].

To create an oxygen-free reaction environment, nitrogen was bubbled into the co-monomer solution for 15 min and a nitrogen blanket over the solution was used for the duration of the polymerization.

After the free-radical polymerization, the emulsion was inversed using POE sorbitol hexaoleate as the inversing agent for activation of the polymer dispersion at a level of 2 to 6w% in the emulsion.

Measurement

Solution viscosities were measured at 25±2°C in a constant temperature water bath with a Brookfield Viscometer, LVTDV-II. The molecular weights of the polymers were determined by viscosimetric measurements using an Ubbelohde viscometer with a capillary diameter of 0.58 mm. Intrinsic viscosities were determined in 1M aqueous solutions of NaCl, 25°C[11].

The sample was titrated to determine the cationicity and degree of branching with anionic potassium polyvinyl sulfate (PPS) in presence of toluidine blue as a cationic dye. The end point was determined, when the color changed from blue to purple.

The cationic charge density (C. E.) was calculated as follows;

$$\text{Cationicity} = \frac{M.V \times 10^{-3}}{5 \times 10^{-3}} \times \frac{1}{400} \times f$$

Where, M. V. denotes the consumption of PPS at the end point and f is the factor of the PPS. The degree of branching was estimated from the relationship between the normal shearing cationicity, the initial point of changing color and high

shearing (1,000 rpm, 5 min), breaking the structure completely.

Flocculation Test

Concentrating sludge was taken from DS sewage plant. The properties of the sludge were 3.1% total solids, conductivity of 0.73 mS/cm, 120 mg/L of $CaCO_3$ hardness, pH 7.46 and 89.1% of organic solids in the total solid.

Before injecting the polymer to flocculate the suspended solids, emulsions were made up to 0.4w% solution using tap water. The water was stirred at 300 rpm and after injecting the polymer, mixing was continued for 30 min, at 200 rpm in a jar-tester. The solution was then aged for another 30 min.

The jar test is a standard method for evaluating the performance of a flocculant. The flocculation is done using 300 mL of sludge in a 500 mL flexible beaker at various rotation speeds, times and polymer dosage. The drainage of flocculated sludge was dewatered using a funnel with a belt filtration membrane and the digital balance was linked with Balancelink from Mettler. Capillary suction time (CST) to estimate the filtration rate was measured using capillary suction timer 304B from Triton Electronics Ltd. This computer recording of the drainage test is estimated since the first 10 to 15 secs of drainage are the most crucial. The dewatering cake was dried at 120±2 ℃ in a dry oven for 4 hr to measure the water content in cake[5].

RESULTS AND DISCUSSION

Polymerization Characteristics

Emulsion flocculants are two phase heterogeneous systems and are comprised of several components. The hydrated polymer is in the shape of microbeads with a 1-micron average diameter. These microbeads are dispersed in the hydrocarbon oil and stabilized by a surfactant to protect against coagulation or agglomeration.

The formulation of a series of partially linear, branched or cross-linked polyacrylamide-co-TMAEAC polymers produced herein is summarized that the

amount of oil phase used was approximately 25~35 wt% depending on the monomer phase condition, the monomer concentration of total charge was 30~45 wt%, and various catalyst and chemicals for generating special structures were in range 0 to 500 mg/L by each polymerization condition.

The other polymerization conditions were the same; the agitation speed was 300±30 rpm, the peak temperature was 60±5 ℃ and the same catalyst system was used in all formulations.

The molecular structure of the flocculant depends on the dewatering performances desired. We estimated the conversion for various cationicities for TMAEAC by drying and extracting the polymer in the emulsion with an acetone/methanol solution and the results are shown in Figure 1.
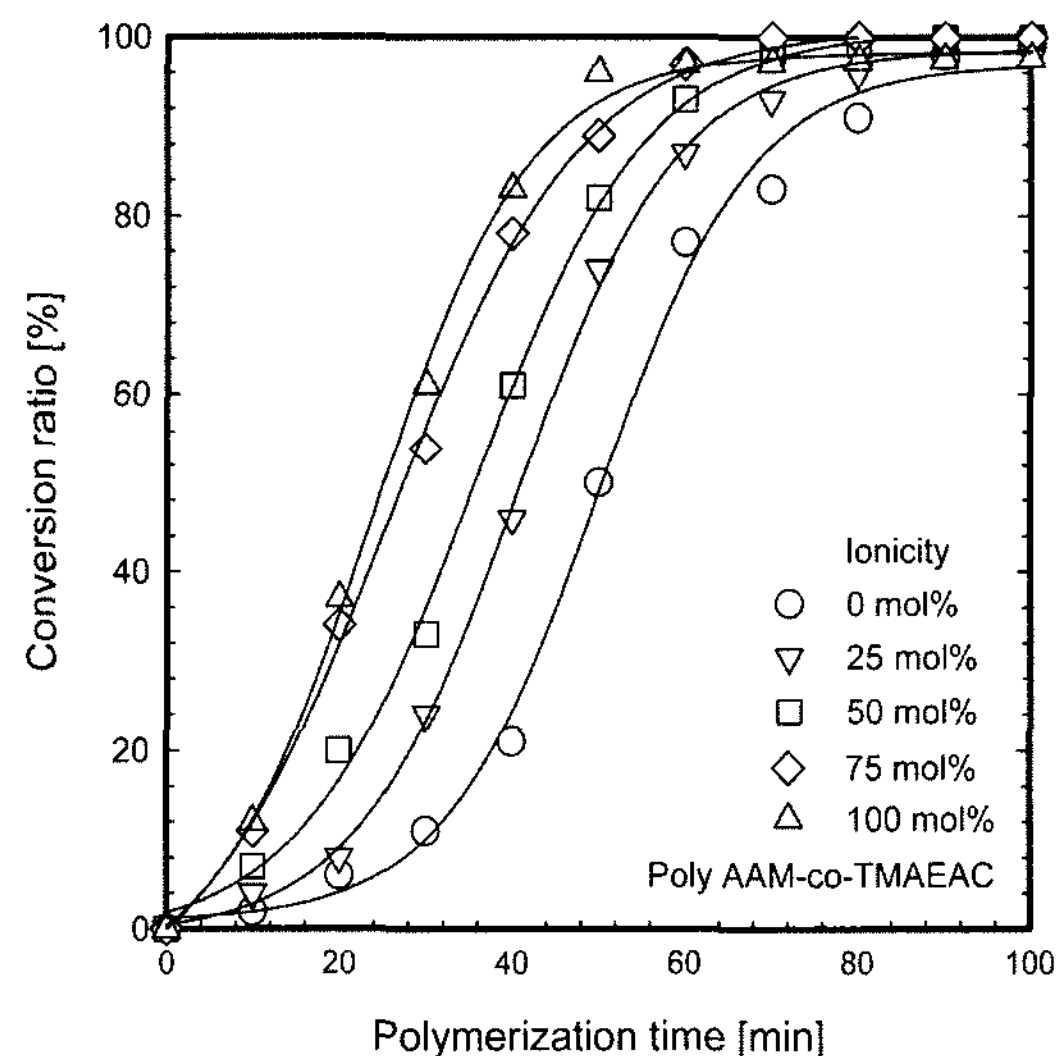

Figure 1. Relationship between conversion ratio and polymer ionicity

As the cationicity of the polymer increases, the conversion rate and ratio of monomer become faster and higher, respectively. This indicates that the acrylamide as nonionic monomer has a lower reactivity than the TAEAC as cationic monomer, under our experimental conditions. The intrinsic viscosity between 20 mol% to 40 mol% the polymer is higher than others. The M. W. of polymers, calculated using Mark - Houwink equation, are range from 5.0×10^6 to 14.0×10^6 Daltons.

The Effect for Amount of Cross-Linking Agent for Polymer

The choice of M.W., which is a measure of the length of the polymer chain, depends on the type of equipment used for the dewatering. For a centrifuge, for example, a high to very high M. W. and branched polymer are best adapted due to the high shearing force applied to the flocs.

Figure 2 reveals the effect of a 20 mol% cationic AAM-co-TMAEAC on the amount of MBA, N, · N-methylene bis-acrylamide, used as cross-linking agent and the properties, such as solution viscosity, degree of branching and viscosity in 1 N NaCl, with molecular weight standard of polymer in the experimental system.
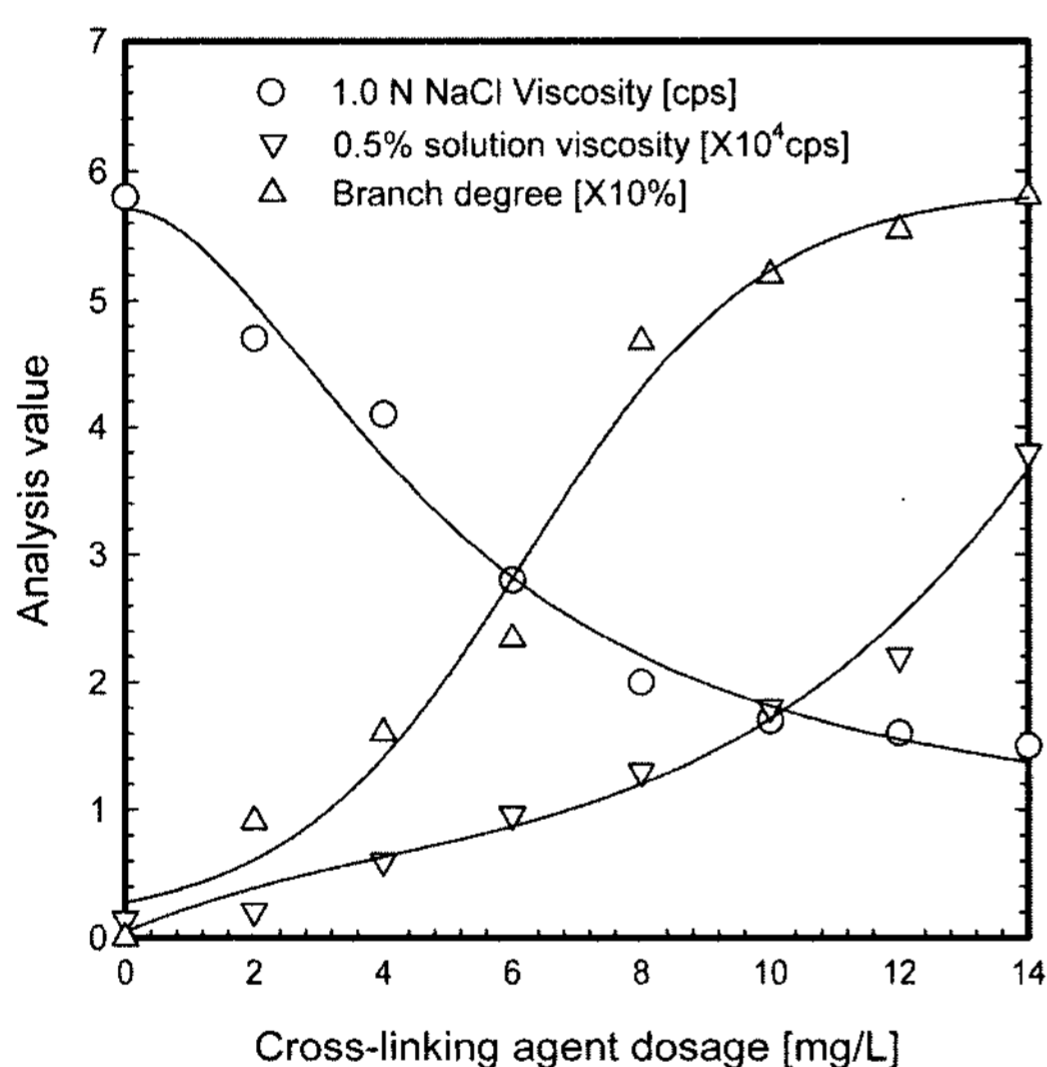

Figure 2. Effect of the amount of MBA and polymer properties in the experimental system.

When the concentration of MBA is more than 12 mg/L, the degree of branching and 1 N NaCl viscosity are maintained, but the viscosity of a 0.5 w% solution increases sharply. In that case, it is very difficult to dissolve the cross-linked polymer and it tends to swell.

The degree of branching and viscosity are proportional to the MBA concentration.

The lower dosage (below 3 mg/L) of MBA in the case of the low cationic polymer leads to a branched polymer. In the case of a less than

cationic 20 mol% polymer, the minimum critical dosage of MBA required to polymerize the branched polymer is more than 4 mg/L, but that for more than 40 mol% cationic polymers is more than 8 mg/L which is based on that the degree of branching is 45%. The optimal amount of MBA to polymerize a branched polymer is 6 ppm.

One of the important properties required for flocculation is a good solubility and stability in water. To improve the solubility of a branched/cross -linked polymer, it is necessary for a good inversion for each polymer particle to be dispersed separately in water. The general amount of inversing agent that has high HLB value for a branched/cross-linked polymer is 1.2 to 1.5 times, for a linear polymer.

Normally the viscosity of polyacrylamide in water is in proportion to its molecular weight. However, a solution of a branched or cross -linked polymer, which has a lower M.W., is more viscous at the same solution concentration. The salt viscosity which is proportional to molecular weight decreases when the amount of MBA is increased from 2 to 12 mg/L. but a higher amount of MBA has no effect on the M. W. of the polymer, because its structure is extensively cross -linked as a super-absorbent[12].

Polymer Stability in the Water

A flocculant is used after dissolving the polymer. Many sewage plants currently use recycle water as polymer dissolving water. Therefore, a polymer in an aqueous solution can be unstable and degradation can result in lower efficiency.

For that reason, the stability of a polymer after dissolving is very important in terms of improving the flocculation efficiency.

We examined the stability of cationic polymer solutions with artificial water of which the pro-perties were 5.0 mS/cm of conductivity, 400 mg/L of $CaCO_3$ hardness, and pH 7.5.

Figure 3 shows the stability of both types of polymers under the same conditions. The viscosities are compared with the original viscosity in deionized water at spindle number 3, 12 rpm, using a Brookfield viscometer. The stability factor
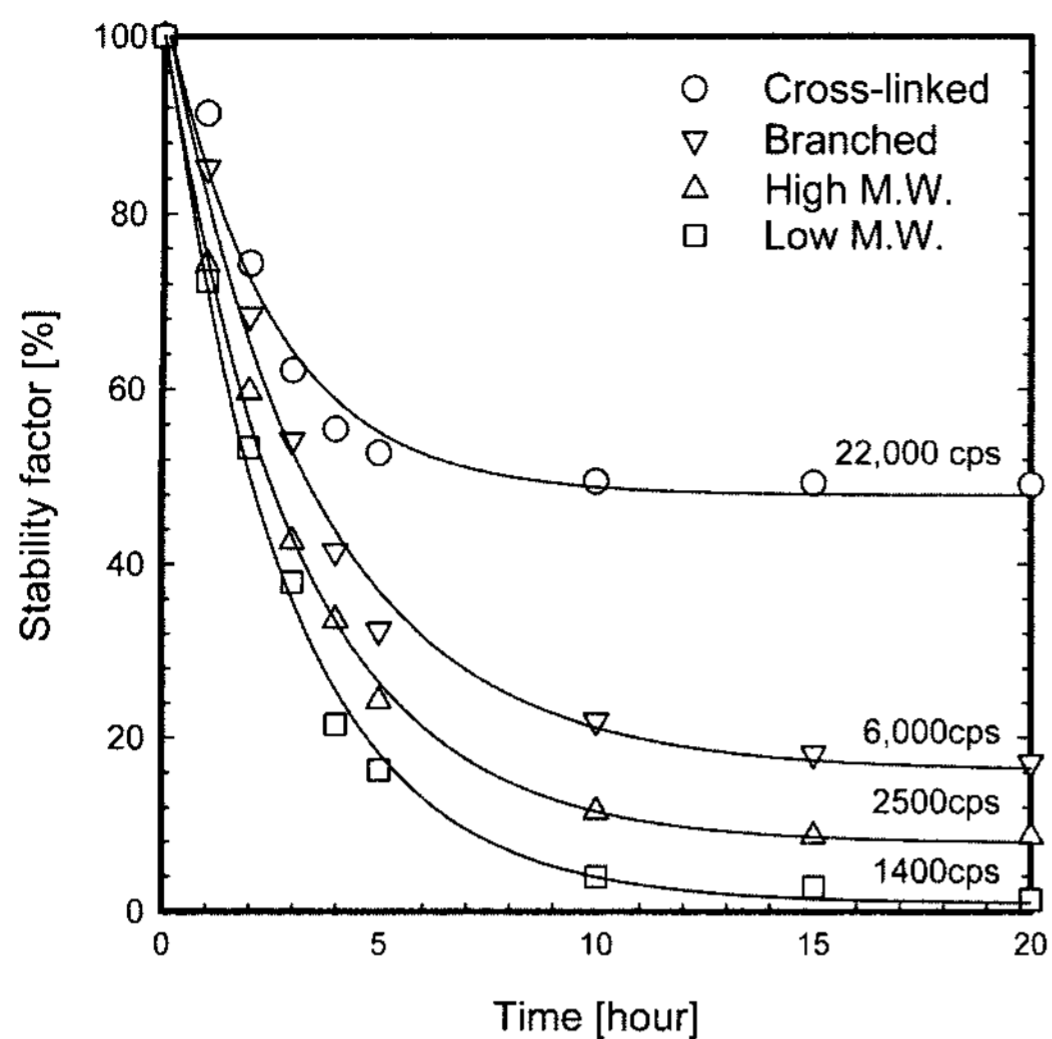
Figure 3. Relationship between the stability of a polymer solution and polymer structures

is measured by the percent of viscosity difference between immediately after dissolving and after storage.

All polymers are 20 mol% cationic and the dissolving concentration is 0.5 wt% for the drainage test.

Cationic polymer solutions are much less stable than those from nonionic and anionic emulsions, because the hydrolysis of the ester function of the cationic functional group occurs. Cationicity, the main factor for flocculation performance not only decreases proportionally with the degree of hydrolysis but very often, depending on the pH and salinity of the water, it may decrease at twice this speed due to interactions between the anionic groups formed through hydrolysis and the unhydrolyzed cationic groups, which is known as a Zwitterion effect. Polyacrylamides in solution are also sensitive to free -radical chain degradation. Free radicals are formed in water by a number of oxidizing and reducing agents; metal ions such as Fe ion and alkali ions[13].

The cross-linked polymer is more stable than a branched or linear polymer of the cationic type. This indicates that the cross-linked polymer is hydrolyzed and degraded only at the external cationic groups and all internal cationic groups

are unreactive. Therefore the stability factor and the drainage efficiency in the case of a cross -linked/branched polymer are much higher than a linear polymer.

Drainage Test for Dewatering Performance

The efficiency of flocculation for separating suspended solids (SS) in water is measured by the size of the flocs and their drainage charac- teristics, the amount of flocculated matter in suspension and the turbidity of the supernatant liquid. In flocculation, three main factors are involved; the molecular weight, the concentration and ionic charge of the polymer itself. We used condensation sludge from DS sewage plant to estimate the performance of the polymers.

We selected the optimum ionic charge by testing all range of cationic polymers with the same molecular weight as shown in Figure 4. The optimum charge and dosage are cationic 20 mol% or 60 mol% and 200~250 mg/L for concen- trated sewage sludge in our experiments. The turbidity of filtrated water using cationic 20 mol% and 60 mol% polymer is 30.3 NTU and 27.8 NTU, respectively.

This computer recording of the drainage test is estimated since the first 10 to 15 secs of the drainage is the most crucial.
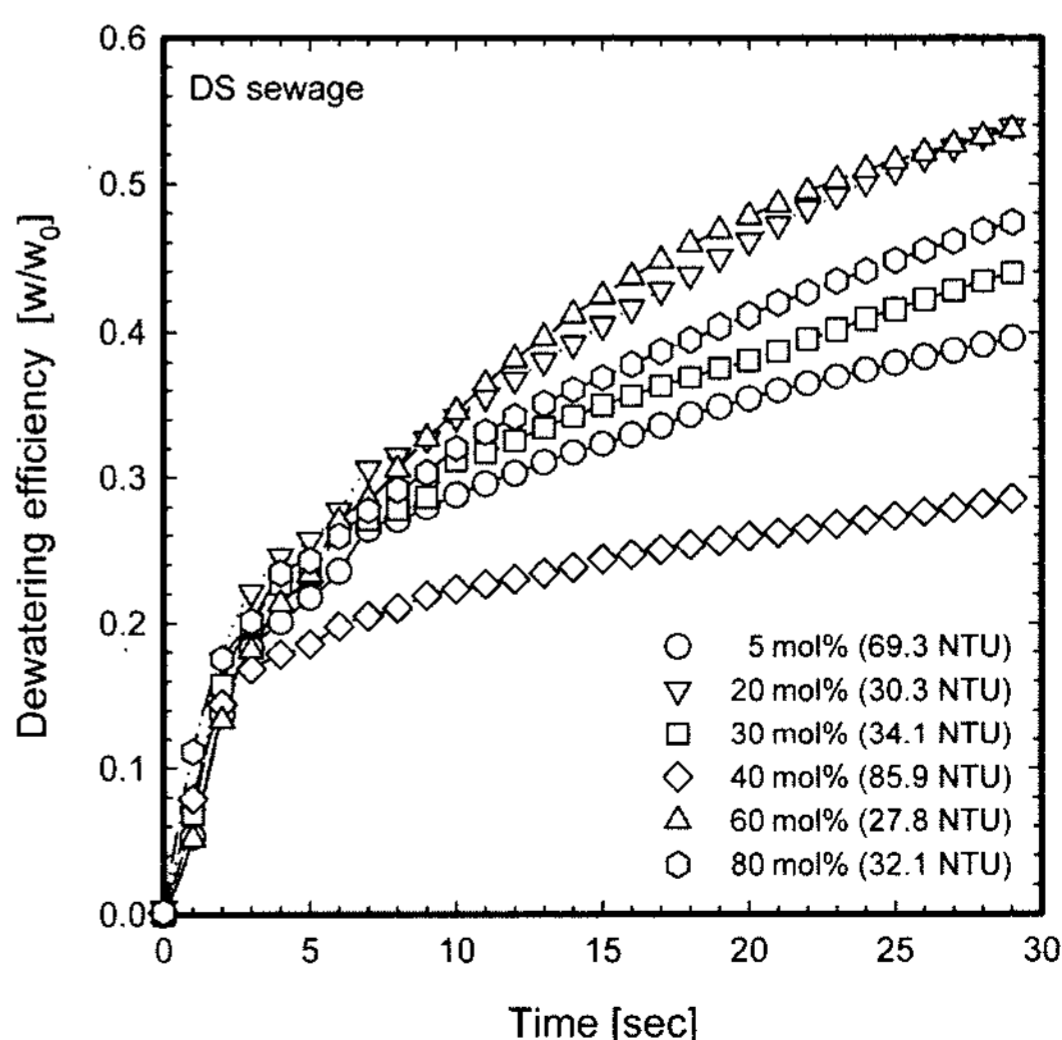

Figure 4. Relationship between the ionicity of a polymer and dewaterability

Figure 5 shows the drainage efficiency for each M. W. and polymer structure for a single flocculation system.
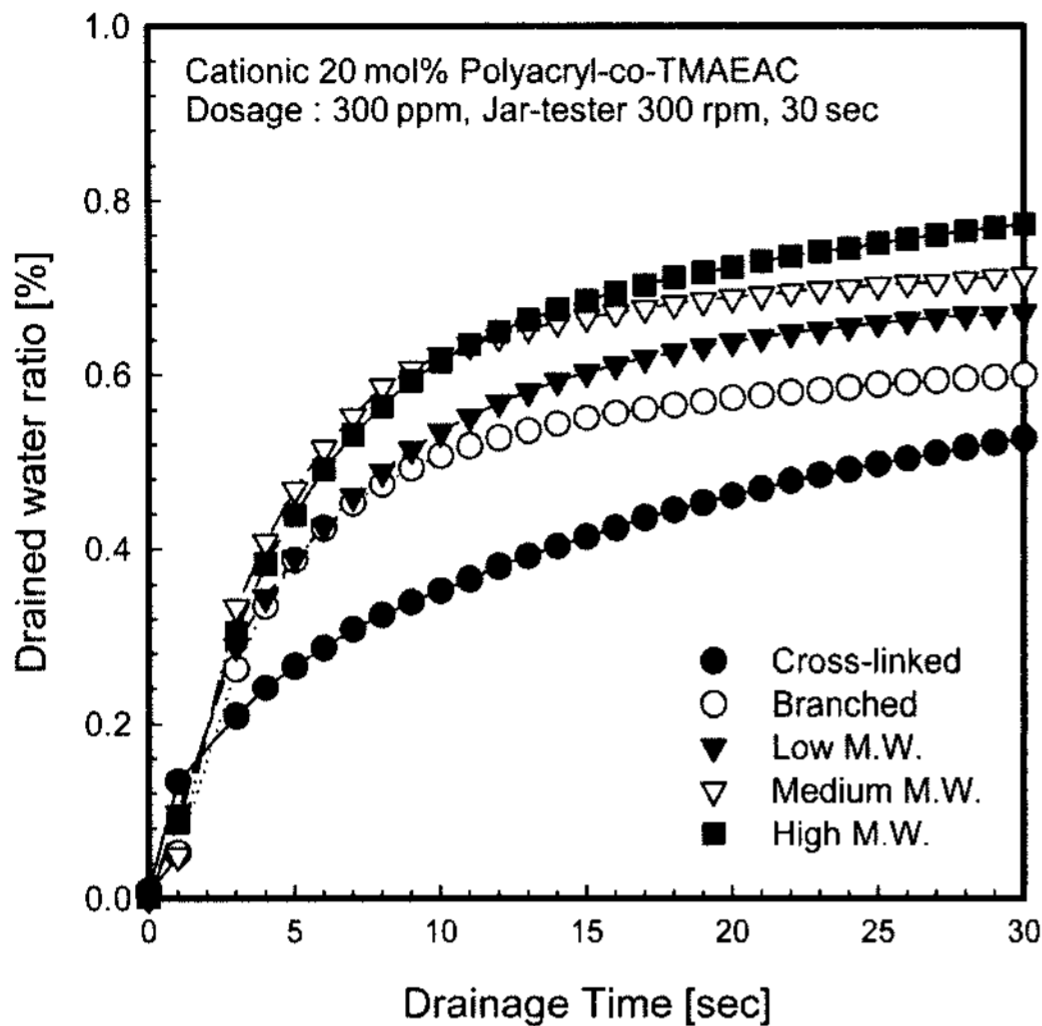

Figure 5. Drainage test result for each molecular weight and polymer structure for general conditions.

The linear polymers have better efficiency than a structured polymer. The efficiency is proportional to the M.W. of polymer. The efficiency of the high M.W. polymer showed an increase of 30% over a cross-linked polymer.

In general, the optimum dosage of branched polymer is 1.5 times higher than that of a linear polymer. However, in high shearing applications such as a centrifuge unit, long-term flocculation, improvement of the water content of cakes and the oxidation of sludge which is difficult to generate a large floc with normal flocculant, and the branched polymer is useful.

The performance as a linear polymer to separate SS is limited by the dosage, because of the residual viscosity in the dewatered cakes. The net charge of the floc in an over-dosage situation is reversed and the floc is restabilized as a result. However, branched polymers don't occurred the viscous cakes in that situation and generate a large floc.

Figure 6 shows the dewatering characteristics of the branched polymer in a dual flocculation system. According to the combination of 1st and

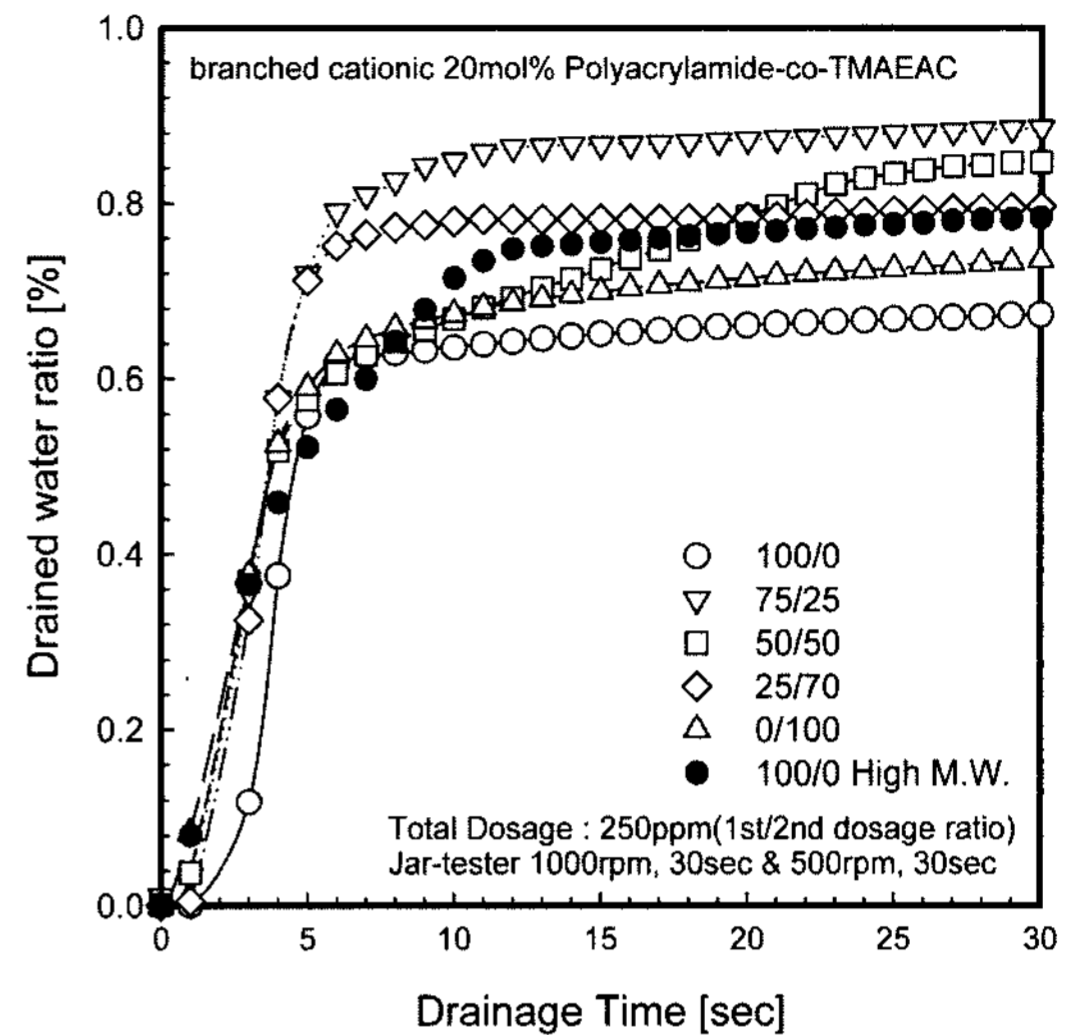2nd dosage, the dewatering characteristics are different from normal flocculation.

Figure 6. Dewatering characteristics of the branched polymer in a dual flocculation system.

The single flocculation by high M. W. polymer has a poor dewatering efficiency compared to the dual flocculation system using branched polymer. For a centrifuge application, the floc must be stronger. The floc generated by a high M. W. polymer is destroyed by excessive shearing. In view of the results so far achieved, the branched polymer on dual flocculation system would be useful for a centrifuge system and other applications. The optimum conditions for improving the efficiency of a flocculant are a dual flocculation system; the 1st and 2nd dosage are 75% and 25% of the total dosage of common flocculation. When the ratio between the 1st and 2nd dosage is 1 over 3 or 3 over 1 in a dual flocculation, the dewatering efficiency is higher than a single flocculation and half in a dual flocculation.

The Mechanism of a Single Flocculant/ Dual Flocculation System

The efficiency of the branched polymer is superior to other polymers in a dual system. The mechanism for this is shown in Figure 7.

In the first step, a large floc is generated by the external cationic functional groups of branched polymer. The floc is then redistributed by long
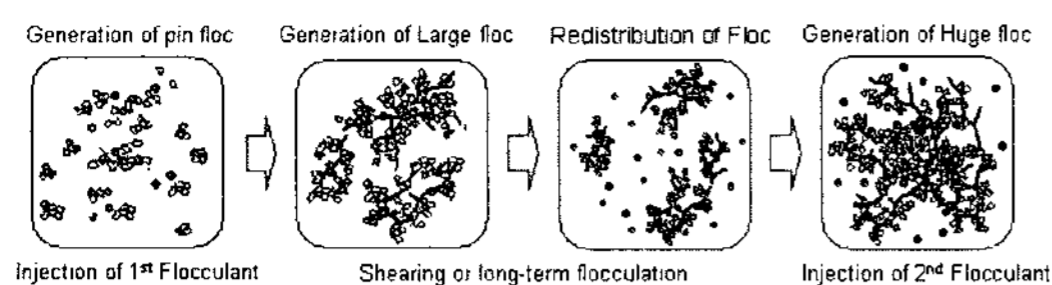
Figure 7. Mechanism of the dual flocculation system for the branched polymer

-term or high shearing forces. Therefore the floc becomes smaller flocs or individual particles. Finally, a huge floc is generated as re-flocculation both of the small flocs occurs by the branched polymer, which has free cationic functional groups in its structures and is used as a post-additional polymer.

As a result, the floc is stronger and larger and the cake has lower water content because the internal water is separated from narrow pores of the pin floc during re-flocculating.

The optimum charge density (C. D.) of a flocculant generates a large floc and removes sources of turbidity. However, an excess C. D. leads to a reverse in the total net charge of the suspended solids in the wastewater and generates viscous dewatered cakes. A low C. D. of flocculant has little active functional groups that generate poor and weak ionic bond. Therefore, the generated floc is easily redistributed. The surface ionicity case of the branched or cross-linked polymer is less than the theoretical ionicity. The structure is in two or three dimensions against the linear polymer, in one dimension.

Therefore, the internal structure contains some ionic functional groups. However, because condensation sludge has a low negative charge in the case of sewage sludge and the shearing speed and force of the decanter is very strong, the branched polymer is available to improve the efficiency for those applications.

The Application of a Single Flocculant/ Dual Flocculation System

Force is created in a conical cylinder bowl in a centrifuge application that rotates at a high speed of 2,500 to 4,000 rpm. The sludge particles are pressed against the bowl and conveyed out of the centrifuge by a screw that rotates at a slightly

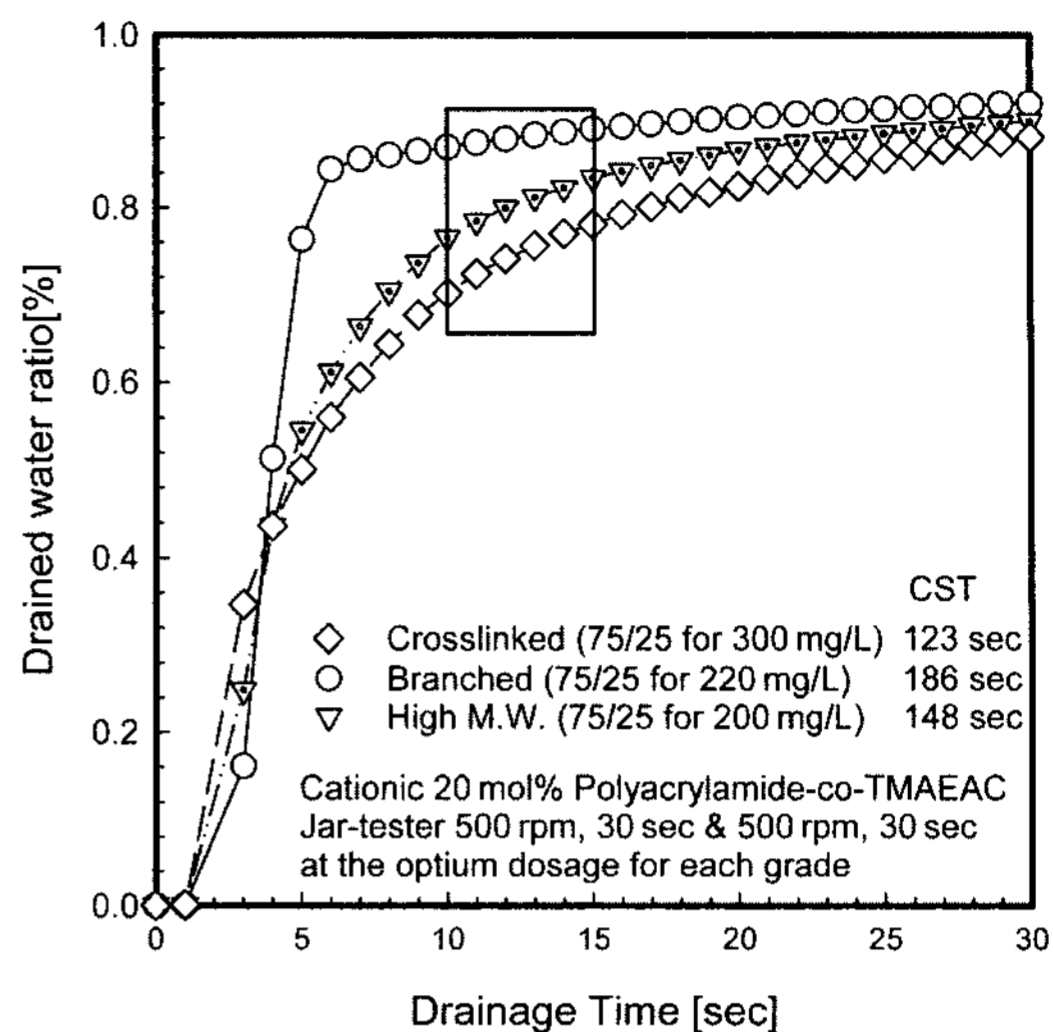different speed than the bowl at a few rpm.

Figure 8. Dewatering characteristics of each polymer in a dual flocculation system.

The initial dewatering rate of a branched polymer in general application, as shown in Figure 8, is very fast. This indicates that the water in the generated flocs is obviously separated by re-flocculation. If the dosage is more than 200 mg/L for a linear high M. W. polymer, the dewatering efficiency is fixed or decreases, due to viscous floc effects.

Although the cross-linked polymer has a high resistance and high viscosity, it has a poor efficiency for dewatering because of the loss of activated functional groups.

To estimate the water content of cake, we measured the CST value of the cakes after the funnel filtration using each polymer. When the branched polymer is used in that condition, the CST value of the dewatered cake is 186 secs and it is lower than others. It expresses the cake adapting with the branched polymer has lower water content in the dewatered cake.

As a result, the dewatering efficiency is improved when the branched polymer is used in a single flocculant/dual flocculation system in high shearing applications, such as a centrifuge unit, long-term flocculation, improvement for water content of cakes and the sludge treated with the advance oxidation treatment.

CONCLUSIONS

To improve the efficiency of a dewatering system, a branched polymer was prepared and the chemical properties and flocculation characteristics were estimated.

The more the cationicity of a polymer, the conversion ratio of the monomer becomes fast and high. This indicates that the nonionic acrylamide monomer has a poorer reactivity than a cationic TAEAC monomer in our experimental conditions.

The cross-linking agent, N,N-methylene bis -acrylamide, decreases the molecular weight when the amount of MBA is increased from 2 to 12 mg/L. But a higher amount of MBA had no effect on the M.W. of the polymer, because its structure is perfectly cross-linked as a super -absorbent. A cross-linked polymer is more stable than branched and linear polymers of the cationic type. This indicates that the cross-linked polymers only the external cationic groups are hydrolyzed and degraded and all internal cationic groups are maintained.

In general, the optimum dosage of a branched polymer is 1.5 times higher than a linear polymer. However, high shearing applications, a branched polymer is more useful and its efficiency is higher than others in a dual system; the optimum conditions for improving the efficiency of a flocculant is a dual flocculation system; 1st and 2nd dosage are 75% and 25% of the total dosage (200~300 mg/L) for common flocculation. In lab test results, the water content of a multi system is less than that of a single system and the sum of the 1st and 2nd dosage is lower than a single system at the same level of performance. If the dosage is more than 200 mg/L in the case of a linear high M.W. polymer, the dewatering efficiency is fixed or decreased.

Although the cross-linked polymer has a high resistance and high viscosity, it has a poor efficiency for dewatering and dosage because of the loss of activated functional groups.

As a result, although the branched polymer polymerized with MBA has poor drainage efficiency in general flocculation, solutions have not only better stability but also a lower water content of dewatered cakes as the result of the re -flocculation effect of dual flocculation. The branched polymer is useful in applications which use recycle water as the dissolving water and lead to a high shearing flocculation.

ACKNOWLEDGEMENTS

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