Flocculation of Clay Suspensions with Water-Insoluble Starch Grafting Acrylamide/Sodium Allylsulfonated Copolymer Powder

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SYNOPSIS

Use of water-soluble and -insoluble starch grafting acrylamide/sodium allylsulfonated copolymers as flocculants to flocculate the clay suspension was investigated. The composition of acrylamide (AM), sodium allylsulfonated (SAS), and starch (St) repeating units in the water-soluble and -insoluble starch-grafted copolymer is about 0.718, 0.022, and 0.260 and 0.439, 0.014, and 0.547, respectively. For the water-soluble starch-grafted copolymer, the fast initial A_r decreasing rate and the lowest final A_r value occur at pH 2, 80 mg/L water-soluble starch-grafted copolymer and 100 mg/L clay suspension. As the suspension contains 1000 mg/L Na^+ ion, the flocculating capability would be increased. For the water-insoluble starch-grafted copolymer, the initial A_r decreasing rate and the final A_r value are 1.6 times and 0.4 times, respectively, that of the water-soluble starch-grafted copolymer at the same test suspension. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The use of polyelectrolytes for removal of clay turbidity from water is the most significant recent development in water technology. The destabilization of colloidal suspensions by organic polyelectrolytes has become increasingly essential in light of their effectiveness in extremely low concentrations. Characteristics of the use of cationic, anionic, and nonionic polymers as coagulant and flocculant for kaolinite suspension have already been investigated.[1,2]

Starch is a naturally low-cost polymer and its derivatives can be used as flocculant in water treatment,[3] such as starch phosphate monoester and tertiary amine or quaternary ammonium etherification of starch, which were applied in the flocculation of aqueous suspensions of clay, titanium oxide, coal, and iron ore particles. The Ce(IV)-induced graft copolymerization of vinyl monomer onto polysaccharide substrates has been used extensively for property modification of naturally occurring polymers.[4-10] Applying the grafting of mixed acrylamide and sulfonate-containing monomers onto corn starch for removal of suspension solid from water has been scarcely investigated.[11] It is found that the flocculation ability of water-soluble starch-grafted copolymer is better than that of the conventional flocculant, partial hydrolyzed polyacrylamide.

Since the settling time of the particle in medium is in inverse proportion to the diameter of a particle, the formed floc by water-insoluble flocculant powder would settle more rapidly than that by the water-soluble flocculant. Thus, using the water-insoluble flocculant would decrease the settling time of the floc and increase the operation efficiency of the flocculation unit in water treatment. Starch can be highly crosslinked with epichlorohydrin or other agents to make it water-insoluble. Chemical modification of the crosslinked starch with various reactive monomers yields ionomer products that can be used as an ion exchanger to remove heavy metal ions from solution in water treatment.[3] We have been shown that the water-insoluble amphoteric starches containing the phosphate or sulfonate anionic group and the quaternary ammonium or ter-

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Journal of Applied Polymer Science, Vol. 58, 1721–1726 (1995)
 CCC 0021-8995/95/101721-06

tiary amine cationic group can remove heavy metal ions from water solution effectively.[12,13] Using the water-insoluble starch ionomer as flocculant to remove the suspension solid from water solution is unavailable in the literature.

This study undertakes the synthesis of a water-insoluble starch grafting acrylamide/sodiumallylsulfonate copolymer powder and the flocculation behaviors between the water-insoluble starch-grafted copolymer and kaolin suspension. Comparison is also made of the flocculation capability among the water-insoluble starch-grafted copolymer, water-soluble starch-grafted copolymer, and pure copolymers.

EXPERIMENTAL

Materials

Corn starch powder (industrial grade) and soluble corn starch (extra pure grade from Merck Chemical Co.) were dried at 105°C before use. Epichlorohydrin, sodium allylsulfonate, acrylamide, and ceric ammonium nitrate (Merck Chemical Co., extra pure) were used as received.

Synthesis of Starch-Grafted Copolymers

Soluble corn starch (32.5 g) was slurried in water (300 mL) in a stirred-glass reaction kettle with a reflux condenser, and heated to 85–90°C until the solution becomes clear and then cooled to 30°C. To this solution, ceric ammonium nitrate initiator (1.1 g) in $1.25 \times 10^{-2} M$ nitric acid aqueous solution (100 mL) was slowly added and stirred for 15 min. Next, a mixture containing acrylamide (54.6 g), sodium allylsulfonated (4.62 g), and water (150 mL) was slowly added, and the mixture was stirred for 4 h at 30°C. The product is the water-soluble starch-grafted copolymer solution.

The resulting copolymer was precipitated by pouring the solution into acetone, followed by washing and drying under reduced pressure to a constant weight. The total monomer conversion was calculated by Eq. (1):

$$\text{conversion} = (W_0 - W_1)/W_2 \qquad (1)$$

where W_0 is the weight of resulting polymer, W_1 is the weight of added starch, and W_2 is the weight of total added monomer. The conversion of the total monomer in the present system is 85%.

The water-insoluble starch-grafted copolymer powder was prepared as in the above process but with crosslinked water-insoluble starch. However, the resulting mixture stood for settling and was separated into two layers, i.e., the upper layer is pure copolymer solution and the lower layer is water-insoluble starch-grafted copolymer powder. The crosslinked water-insoluble starch was prepared by taking the diameter between 30 and 65 mesh corn starch powder reacted with epichlorohydrin. The crosslinking procedures of the corn starch powder are the same as that described in our previous work.[12]

Flocculation Experiments

Flocculation experiments were carried out by adding flocculant to a 500 mL, 100 ppm kaolin clay suspension. The suspension is prepared at the desired initial pH and concentration of NaCl or Na_2SO_4. The initial pH of suspension was adjusted with $0.1N$ NaOH aqueous solution and $0.1N$ HCl aqueous solution. As the desired amount flocculant was added, the solution was stirred at 100 rpm for 2 min and then was stirred at 25 rpm for 25 min. The optical absorbance of suspension at the half of height below the water surface was determined periodically. The relative absorbance (A_r) is the ratio of absorbance of suspension at each period settling time (A_t) to that at the initial settling time (A_0).

The A_r value of each point on the settling curves is the average value of 10 data under the same test condition. These data are located in 95% confidence region as determined by statistical analysis. Two examples of settling curves with error-bar are shown in Figure 2(a). The control settling curve [shown in Fig. 2(b)] is the sedimentation of kaolin suspension in the absence of the starch-grafted copolymer flocculant, Na_2SO_4 and NaCl.

Measurements

The amount of C, H, and N elements in the water-soluble and water-insoluble starch-grafted copolymer was measured using a Model CHN-O-RAPID elemental analyzer from Heraeous Company. The amount of S element in the water-soluble and water-insoluble starch-grafted copolymer was measured using a Model COULOMAX 78 elemental analyzer from Tacussel Company. The optical absorbance of solution was measured using a Model 2000 optical analyzer from Merck Company.

Table I Characteristic Analysis of Starch-Grafted Copolymer

Sample	Elemental Analysis, wt %							
	C	H	N	S	F_{Am}	F_{Sas}	F_{St}	W_g
Water-soluble starch-grafted copolymer	39.39	7.01	10.50	0.745	0.718	0.022	0.260	0.563
Water-insoluble starch-grafted copolymer	39.97	6.94	5.05	0.370	0.439	0.014	0.547	0.273

RESULTS AND DISCUSSION

Flocculant Characteristic Analysis

The weight percentage of the C, H, N, and S elements in the water-soluble and water-insoluble starch-grafted copolymers are listed in Table I. The grafted copolymer compositions and weight fraction of grafted chains were calculated using the following equations:

$$\%N = \frac{14F_{Am}}{162F_{St} + 71F_{Am} + 144F_{Sas}} \times 100\% \quad (2)$$

$$\%S = \frac{32F_{Sas}}{162F_{St} + 71F_{Am} + 144F_{Sas}} \times 100\% \quad (3)$$

$$F_{St} + F_{Am} + F_{Sas} = 1.0 \quad (4)$$

$$W_g = \frac{71F_{Am} + 144F_{Sas}}{162F_{St} + 71F_{Am} + 144F_{Sas}} \quad (5)$$

where F_{St}, F_{Am}, and F_{Sas} are the mole fraction of starch, acryamide, and sodium allylsulfonate repeating units, respectively. W_g is the weight fraction of grafted chains in grafted copolymer. The values of F_{St}, F_{Am}, F_{Sas}, and W_g calculated by the above equations are listed in Table I. The values of F_{Am}, F_{Sas}, F_{St}, and W_g of water-soluble and water-insoluble starch-grafted copolymer are 0.718, 0.022, 0.260, and 0.563 and 0.439, 0.014, 0.547, and 0.273 respectively. Those results indicate that the degree of grafted-copolymer onto the water-insoluble starch is lower than that onto the water-soluble starch. The reason for this occurrence is that the graft reaction is a heterogeneous reaction for water-insoluble starch and a homogenous reaction for water-soluble starch.

Flocculation Test

Now, we take the water-soluble and water-insoluble starch-grafted copolymer, and pure copolymer as three types of flocculants. A comparison of the flocculating capability among the three types flocculants was made. First, the flocculation behaviors of the water-soluble starch-grafted copolymer flocculant were investigated at various initial pH of suspension and concentration of flocculant and salts to determine the optimum flocculating condition.

Effect of pH

The relationship of relative absorbance (A_r) with time for the initial pH of suspension ranging from 2 to 8 in the 80 mg/L water-soluble starch-grafted copolymer flocculant and 100 mg/L kaolin suspension is shown in Figure 1. The value of A_r decreases rapidly at the initial settling time (about 10 min), and then it almost remains constant. This figure indicates that the initial A_r decreasing rate increases and the final A_r value decreases as the initial pH of suspension decreases. Furthermore, the results reveal that the solution at pH 2 has the highest floc-

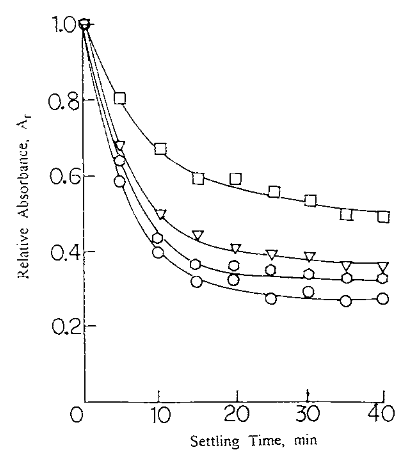

Figure 1 The relationship of A_r with time at various initial pH of suspension in 80 mg/L water-soluble starch-grafted copolymer and 100 mg/L kaolin suspension: (O) pH 2, (O) pH 4, (▽) pH 6, and (□) pH 8.

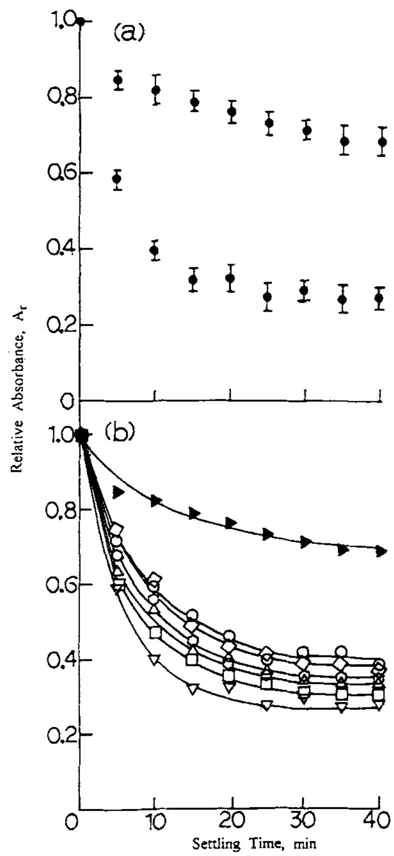

Figure 2 The relationship of A_r with time at various concentration of water-soluble starch-grafted copolymer in pH 2 and 100 mg/L kaolin suspension: (a) with error-bar, 0 mg/L and 80 mg/L; (b) (▶) 0 mg/L, (○) 50 mg/L, (△) 60 mg/L, (□) 70 mg/L, (▽) 80 mg/L, (o) 90 mg/L, (◇) 100 mg/L.

culating capability. Thus, pH 2 was selected here as the test condition for the later experiment.

Concentration of Flocculant

The relationship of A_r with time for the concentration of water-soluble starch-grafted copolymer flocculant range from 0 to 100 mg/L in the pH 2 and 100 mg/L kaolin suspension is shown in Figure 2. This figure indicates that the initial A_r decreasing rate increases as the concentration of flocculant increases from 0 to 80 mg/L and, then, it decreases as the concentration of flocculant increases from 80 to 100 mg/L. This result reveals that having an optimal concentration of flocculant appears to be the most effective flocculation. This is because the larger amount of flocculant in the suspension causes a larger amount of suspended particle to aggregate and settle. However, an over optimal amount of flocculant in the suspension would cause the aggregated particle to redisperse in the suspension and would

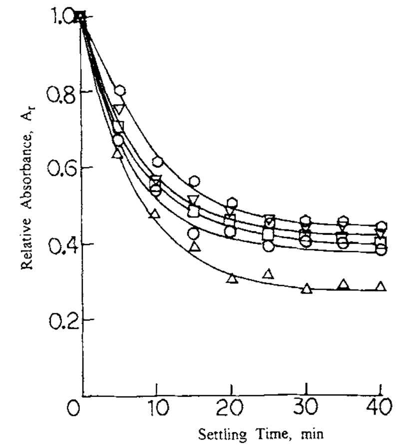

Figure 3 The relationship of A_r with time at various concentration of Na_2SO_4 in pH 2, 80 mg/L water-soluble starch-grafted copolymer and 100 mg/L kaolin suspension: (○) 0 mg/L, (△) 500 mg/L, (□) 1000 mg/L, (▽) 3000 mg/L, (o) 6000 mg/L.

also disturb the particle settling. The lowest final A_r value is equal to 0.28 at the concentration of flocculant 80 mg/L. The final A_r value and the initial A_r decreasing rate of control suspension are higher and slower than those having flocculant suspensions, respectively. The result reveals that the starch-grafted copolymer has flocculation capability.

Effect of Salts

The relationships of A_r with time for the concentration of Na_2SO_4 or NaCl range from 0 to 6000 ppm

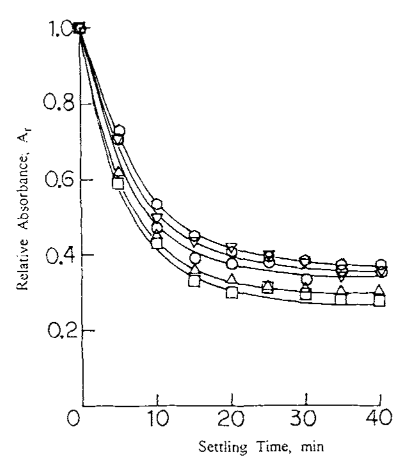

Figure 4 The relationship of A_r with time at various concentration of NaCl in pH 2, 80 mg/L water-soluble starch-grafted copolymer and 100 mg/L kaolin suspension: (○) 0 mg/L, (△) 500 mg/L, (□) 1000 mg/L, (▽) 3000 mg/L, (o) 6000 mg/L.

in the pH 2, 80 mg/L water-soluble starch-grafted copolymer flocculant and 100 mg/L kaolin suspension are shown in Figures 3 and 4. These figures reveal that the maximum initial A_r decreasing rate and the lowest final A_r value occurred at the concentration of Na_2SO_4 500 mg/L and of NaCl 1000 mg/L. Adding salt into the kaolin suspension would compress the electronic double layer around the particle as well as inhibit the polymer chain of flocculant extension.[14] The former is favorable to particle aggregation and flocculation; in addition, the later is unfavorable to the adsorption and interparticle bridge between particle and flocculant. Thus, an optimal salt concentration appears to be the most effective flocculation.

At the most effective flocculation, the concentration of salts in solution is 500 ppm for Na_2SO_4 and 1000 ppm for NaCl. Both solutions contain 1000 ppm Na^+ ion. This fact implies that the coexisting ion (Na^+) would affect the flocculation capability of the flocculant because the flocculant is a sodium salt ionomer.

Comparison the Flocculation Capabilities among Water-Soluble Starch-Grafted Copolymer, Water-Insoluble Starch-Grafted Copolymer, and Pure Copolymer Flocculants

To understand the flocculation capabilities among the three types of flocculants (water-soluble starch-grafted copolymer, water-insoluble starch-grafted copolymer, and pure copolymer), the pH 2 and 100 mg/L kaolin suspension was selected here as the test suspension. The amount of each type of flocculant added must maintain the concentration of Sas repeating unit in the suspension to that of the 80 mg/L water-soluble starch-grafted copolymer in the suspension. All these conditions are verified to lead to the most effective flocculation from the above results.

The relationship of A_r with time for the three types of flocculants is shown in Figure 5. The initial A_r decreasing rate and the final A_r value are found to be in the order water-insoluble starch-grafted copolymer > pure copolymer > water-soluble starch-grafted copolymer. The initial A_r decreasing rate of water-insoluble starch-grafted copolymer is approximately 1.6 times that of the water-soluble starch-grafted copolymer. The final A_r values are 0.12, 0.25, and 0.28 for the water-insoluble starch-grafted copolymer, pure copolymer, and water-soluble starch-grafted copolymer, respectively. Those results indicated that the flocculation capability of water-insoluble starch-grafted copolymer is roughly

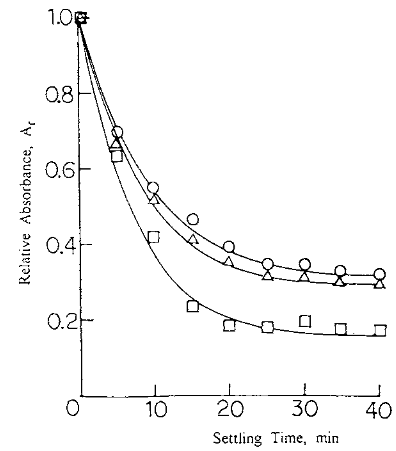

Figure 5 The relationship of A_r with time for three types flocculant in pH 2, 80 mg/L flocculant and 100 mg/L kaolin suspension: (○) water-soluble starch-grafted copolymer, (□) water-insoluble starch-grafted copolymer, (△) pure copolymer.

double that of water-soluble starch-grafted copolymer. Since the water-insoluble starch-grafted copolymer is a water-insoluble powder, the formed floc by water-insoluble starch-grafted copolymer has the largest density among the three types of flocculants. Therefore, the formed floc by water-insoluble starch-grafted copolymer has the shortest settling time. Furthermore, the scrapping effect would occur during the formed floc by water-insoluble starch-grafted copolymer settling; in addition, the effect would cause the smaller particle to be settled. Thus, the flocculation capability of water-insoluble starch-grafted copolymer is higher than that of the other two flocculants.

CONCLUSION

High crosslinked water-insoluble starch grafting acrylamide/sodium allylsulfonated copolymer powder can be used to flocculate the clay suspension. The composition of acryamide (AM), sodium allylsulfonated (SAS), and starch (St) repeating units in water-soluble and water-insoluble starch-grafted copolymer is about 0.718, 0.022, and 0.260 and 0.439, 0.014, and 0.547, respectively. For the water-soluble starch-grafted copolymer, the fast initial A_r decreasing rate and the lowest final A_r value occur at pH 2, 80 mg/L water-soluble starch-grafted copolymer and 100 mg/L clay suspension. As the suspension contains 1000 mg/L Na^+ ion, the flocculating capability would be increased. For the water-insoluble starch-grafted copolymer, the initial A_r decreasing rate and the final A_r value are 1.6 times and 0.4 times, respectively, that of the water-soluble starch-grafted copolymer at the same test suspension.

The authors thank the National Science Council of the Republic of China for financial aid throughout the project (NSC-83-0115-C-216-0002).

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Received October 8, 1994
Accepted May 10, 1995