

An Investigation of the Flocculation Characteristics of Polyacrylamide-Grafted Chitosan

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ABSTRACT: To investigate the flocculation characteristics of polyacrylamide (PAM)-grafted chitosan, a series of PAM-grafted chitosan copolymer (Chito-g-PAM1 to Chito-g-PAM4) have been synthesized by ceric ammonium nitrate-induced solution polymerization technique in nitrogen atmosphere. The flocculation characteristics of the polymer samples (PAM, grafted and ungrafted chitosan) were studied by settling test and jar test methods in the colloidal suspensions of kaolin, iron ore, silica, and ben-

tonite powder. It was found that the settling performance of Chito-g-PAM3 is best among the polymer samples. The jar test results indicate that the ungrafted chitosan has better water clarifying performance than both the PAM and grafted chitosan. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 2410–2414, 2009

Key words: flocculation; polysaccharide; polyacrylamide; graft copolymer; colloid

INTRODUCTION

The removal of contaminants from effluents before discharging them into the environment is a serious problem faced by many industries. Inorganic coagulants such as alum in combination with lime have been conventionally used for many years for the removal of contaminants from raw water.^{1–3} Stauber et al.⁴ and McLachlan⁵ have reported that the residual aluminum, which may be present in the water as a result of the alum treatment, may cause Alzheimer's disease. These inorganic coagulants are required in a large quantity to remove the contaminants from water. The large volume of sludge formed from such treatment faces health threats and disposal problem. Thus, it becomes necessary to develop more efficient, harmless, and environment friendly material for the removal of the colloidal particles from the aqueous suspension. Synthetic polymers such as polyacrylamide (PAM) and its derivatives have been commercially used as flocculant for the removal of the contaminants.^{6,7} However, these synthetic polymers are nonbiodegradable and unstable to shear field,^{8–11} and these attribute limit their effective application as flocculant.

On the other hand, natural polymers such as polysaccharides are biodegradable and resistant to shear

degradation,¹² but they are less effective as flocculant. To get a synergistic effect of both the synthetic polymers and polysaccharides, grafting of PAM onto the backbone of polysaccharides has been proposed.^{13,14} In our laboratory, intensive investigations have been carried out to graft PAM onto the backbone of various polysaccharides.^{15–21} It has been observed that the graft copolymers show better flocculation efficiency than that of ungrafted polymer. Singh¹² suggested that this enhancement of the flocculation efficiency is due to the closer approachability of the PAM side chains to the suspended particles.

In this study, chitosan has been used as polysaccharide, and PAM has been grafted onto its backbone. Chitosan is a biopolymer, extracted from chitin by deacetylation in the presence of alkali.²² Chitin is a hard, inelastic nitrogenous polysaccharide extracted from crustacean shells, such as prawns, crabs, insects, and shrimps.^{23,24} Chitosan draws attention because of its higher percentage of nitrogen content. The amine and hydroxyl groups on its backbone act as chelating sites for metal ions.²³ Studies have found that chitosan acts as an excellent flocculating material for the adsorption of metal ions from aqueous suspensions.^{25,26} It is also biocompatible, nontoxic, and biodegradable.

In this part of our research, the flocculation characteristics of the grafted chitosans (Chito-g-PAM1 to Chito-g-PAM4) have been investigated and compared with PAM and ungrafted chitosan in aqueous suspensions of kaolin, iron ore, silica, and bentonite powder.

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TABLE I
Synthesis Details of PAM-Grafted Chitosan

Grafted Chitosan	Chitosan (mole in MSU ^a)	Acrylamide (mole)	Amount of CAN mole $\times 10^{-3}$	Intrinsic Viscosity ^b (dL/g)
Chito-g-PAM1	0.005	0.30	1.8	3.453
Chito-g-PAM2	0.005	0.20	0.126	5.625
Chito-g-PAM3	0.005	0.20	0.090	8.09
Chitp-g-PAM4	0.005	0.20	0.054	7.598

^a Monosaccharide units (MSU).

^b Intrinsic viscosity is measured by Ubbelohde viscometer at 30°C.

EXPERIMENTAL

Materials for the preparation of grafted chitosan

Chitosan was a gift from the Central Institute of Fisheries Technology, Cochin, India. Acrylamide (AM) was obtained from E. Merck, Darmstadt, Germany. Ceric ammonium nitrate (CAN) was obtained from Loba Chemie, Mumbai, India. Acetone, hydroquinone, and acetic acid were obtained from S.D. Chemicals, Mumbai, India.

Materials for the colloidal suspensions

Kaolin powder was supplied by B.D. Pharmaceutical Works, Howrah, India. Iron ore powder was obtained from Joda Mines, Orissa, India. Silica powder was obtained from Jyoti Chemicals, Mumbai, India. Bentonite powder was obtained from Merck Limited, Mumbai, India.

Synthesis of the PAM-grafted chitosan

PAM-grafted chitosan copolymers were synthesized by solution polymerization technique using CAN as redox ion initiator in nitrogen atmosphere.²⁷ Chitosan was first dissolved in 1% acetic acid solution in a three-necked round bottomed flask. The flask was placed on a thermostat fitted with a magnetic stirrer to control the reaction temperature and mixing speed. The mixture was heated at 33°C with controlled stirring. Desired amount of AM was then added to the mixture. The mixture was stirred at a moderate speed for 5 min. While stirring, nitrogen gas was passed into the mixture to remove the dissolved oxygen. After passing nitrogen for 25 min, freshly prepared aqueous solution of CAN was added to the reaction mixture. The stirring was continued for another 15 min to mix the CAN homogeneously. The stirring and passing of nitrogen were stopped, and the reaction was allowed to continue for next 24 h. Aqueous solution of hydroquinone was added to the mixture to terminate the reaction. The mixture was then poured into distilled water to make slurry. Then, the slurry was poured in excess of acetone to precipitate the product completely. The

product was filtered and washed with acetone for several times. The filtered product was dried in vacuum oven at 55°C for 2 h. Subsequently, it was pulverized and sieved. The graft copolymers were further purified by solvent extraction technique,²⁸ with a mixture of formamide and acetic acid (1 : 1, v/v). In the similar way, a series of PAM-grafted chitosan copolymers (Chito-g-PAM1 to Chito-g-PAM4) was synthesized. The details of the synthesis are summarized in Table I.

Preparation of the stock solution for flocculation study

Calculated amount of the polymer sample was mixed with definite volume of 1% acetic acid solution. The dissolution is slow, so the mixture was stirred on magnetic bath at a constant speed of 100 rpm until the polymer dissolved properly. Before each set of experiment, the stock solutions were made freshly for consistency. It should be noted here that the stock solutions could be stored in closed dark bottles for many days and it will improve the flocculation efficiency. This increase in efficiency may be attributed to the weakening of the association between the polymer chains with time. The stock solutions were diluted with freshly prepared distilled water to get the solution of desired concentration.

Preparation of the colloidal suspension for flocculation study

Aqueous suspension of the colloidal particles was prepared by mixing desired amount of the colloidal powder in distilled water.

Flocculation studies

The flocculation characteristics of the polymer samples were studied by settling test and jar test methods.

Settling test

The settling test is one of the most common methods to investigate the flocculation efficiency. The settling

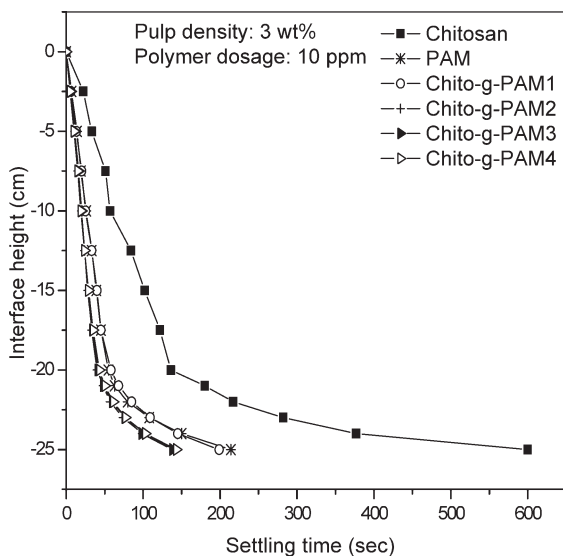


Figure 1 Settling behavior of kaolin suspension with various grades of polymer solutions.

test comprises a 100-mL stoppered graduated cylinder and a stopwatch. In the settling test method, first the aqueous suspension of the colloidal particles is taken into the cylinder, and then the calculated volume of polymer solution is added to the suspension. The cylinder is stoppered and the whole system is carefully inverted 10 times for thorough mixing. Then, the cylinder is kept upright, and the interface height of the concentrated settling solid and supernatant water is measured with time.

Jar test

A conventional jar test apparatus comprises a flocculator and a turbidity meter. The flocculator was supplied by M.B. Flocculator, Mumbai, India. It consists of six equal size pedals on a bench, connected to each other by a gear mechanism. The flocculator has a provision of speed control. An aqueous suspension of 400 mL is taken in each 1-L beaker, and a calculated volume of polymer solution is added to it. The mixture is initially stirred for 2 min at a constant speed of 75 rpm. At this speed of mixing, the polymer solution is properly mixed in the aqueous suspension. The stirring speed is then lowered to 25 rpm, and the whole mixture is stirred at this particular speed for next 5 min. At this speed of mixing, the polymers get adsorbed onto the suspended particle surface, and then large voluminous flocs are formed. The flocs are then allowed to settle for next 10 min. Then, the supernatant liquid from each of the beaker is carefully withdrawn and their turbidity is measured by a precalibrated digital nephelo turbidity meter. The turbidity is expressed in nephelo turbidity unit (NTU). A series of jar test was conducted to study the water clarifying performance of

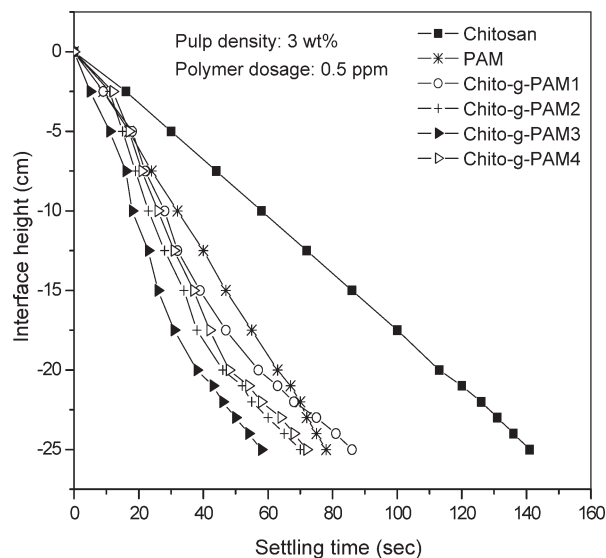


Figure 2 Settling behavior of iron ore suspension with various grades of polymer solutions.

the polymer samples by keeping other parameters constant.

RESULTS AND DISCUSSION

Settling test

The settling test investigates how fast a flocculant can remove colloidal particles from the suspension. It is believed that the higher the settling velocity of the flocs, the better is the flocculating performance of the flocculant. The settling velocity of a particular suspension at a particular concentration can be obtained by drawing the greatest tangent on the interface height versus settling time profile for a

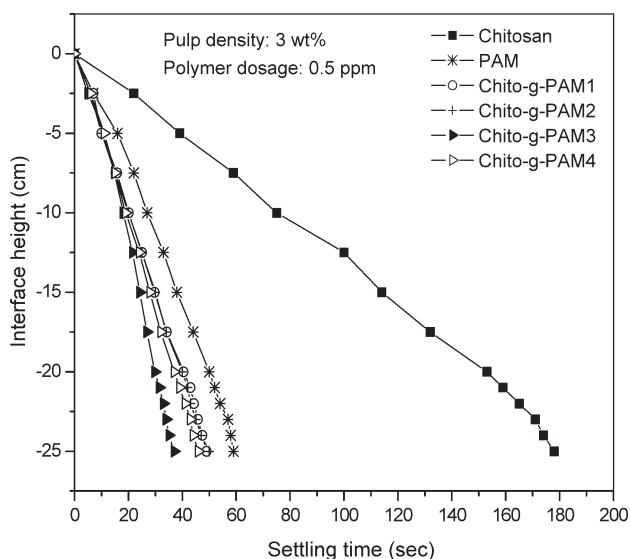


Figure 3 Settling behavior of silica suspension with various grades of polymer solutions.

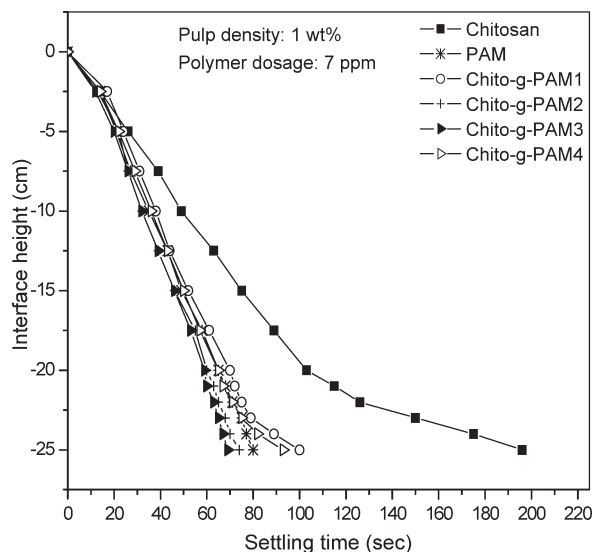


Figure 4 Settling behavior of bentonite suspension with various grades of polymer solutions.

chosen colloidal suspension. The concentration of the flocculant is a key parameter to achieve efficient flocculation. The polymer dosages typically used for this investigation are in the order of parts per million (ppm). Figures 1–4 show the settling velocity of kaolin, iron ore, silica, and bentonite suspensions, respectively. These figures (Figs. 1–4) show that the settling performance of Chito-g-PAM3 is best among the polymer samples. The best settling performance of Chito-g-PAM3 may be due to the presence of fewest but longest PAM side chains onto the backbone of chitosan, which bridges largest number of colloidal particles before flocculate them. The presence of longest PAM side chain in Chito-g-PAM3 is reflected from its highest intrinsic viscosity value (Table I).

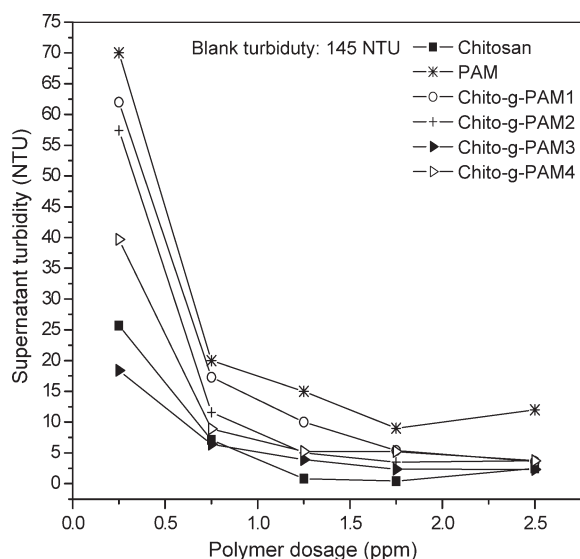


Figure 5 Jar test results of 0.25 wt % kaolin suspension with various grades of polymer solutions.

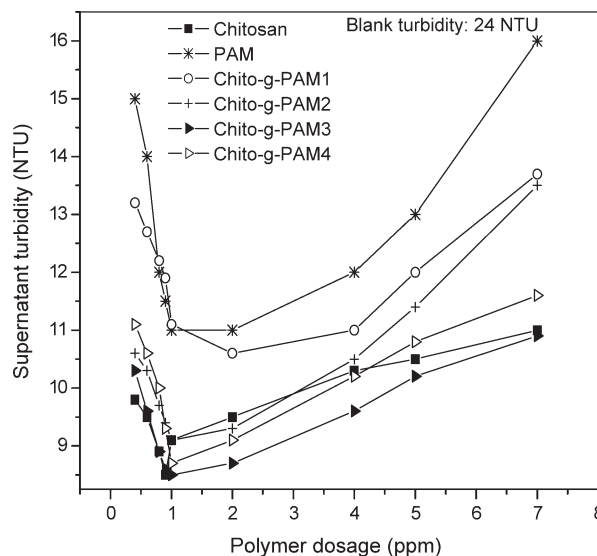


Figure 6 Jar test results of 0.25 wt % iron ore suspension with various grades of polymer solutions.

Jar test

The jar test investigates how far the flocculants can clarify the colloidal suspension. In this case, the turbidity of the supernatant liquid after a fixed time is plotted against the polymer dosage. The jar tests were carried out at 0.25 wt % of the colloidal suspensions at various polymer dosages. Figures 5–8 represent the jar test results of all the polymer samples. It is evident from the jar test results (Figs. 5–8) that though the water clarifying performance of Chito-g-PAM3 is better among the grafted grades, its water clarifying performance is inferior to the ungrafted chitosan. The superior water clarifying performance of ungrafted chitosan may be due to the

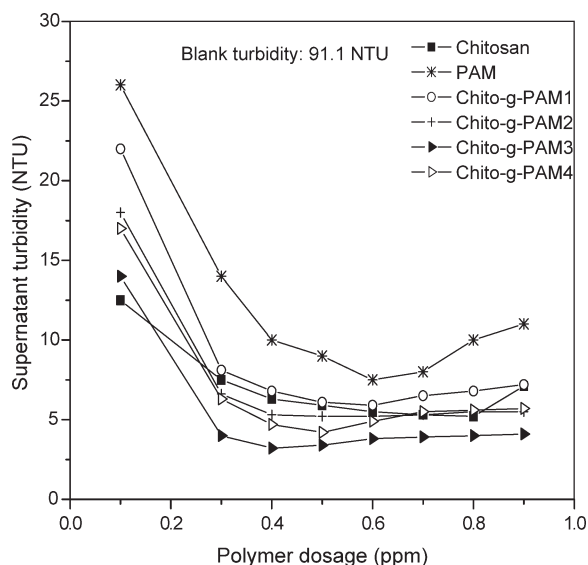


Figure 7 Jar test results of 0.25 wt % silica suspension with various grades of polymer solutions.

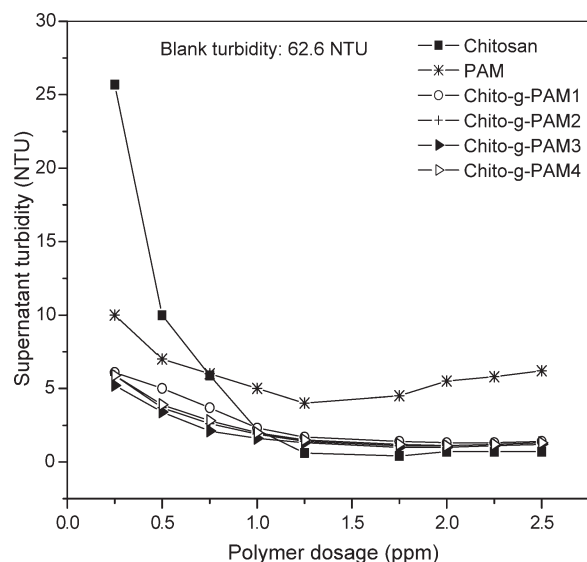


Figure 8 Jar test results of 0.25 wt % bentonite suspension with various grades of polymer solutions.

presence of amine groups into the backbone of chitosan, which has greater affinity toward metal ions. Chitosan makes smaller but stronger flocs, which settle slowly with time. On the other hand, grafted chitosan forms larger but relatively loose flocs with its long PAM side chains, which settle rapidly. During rapid settling, some portion of the floc breaks. These small flocs remain suspended for long time in the aqueous medium and increase the turbidity value of the supernatant liquid. The jar test results (Figs. 5–8) also show that after an optimum polymer dosage, the addition of excess polymer increases the turbidity value of the supernatant liquid. This may be due to the deflocculation effect by the presence of excess polymer in the solution.

CONCLUSIONS

From these investigations, it can be concluded that chitosan itself is a good flocculating material. By the incorporation of the PAM moiety onto its backbone, a modified flocculating material can be developed for the treatment of wastewater. The polymer dosage required to achieve effective flocculation is very low

and it is in the order of ppm level. From the settling tests it can be concluded that Chito-g-PAM3 shows best settling performance in all the colloidal suspensions. The results of the jar test concluded that the water clarifying performance of ungrafted chitosan is better than both the PAM and grafted chitosan.

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