Investigation on Flocculation Characteristics of Polysaccharide-Based Graft Copolymers in Coal Fines Suspension

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ABSTRACT: The article deals with the synthesis of two polysaccharide-based graft copolymers of acrylamide, namely, starch-*g*-polyacrylamide (St-*g*-PAM) and amylopectin-*g*-polyacrylamide (Ap-*g*-PAM). Intrinsic viscosity of the graft copolymers was determined. A flocculation jar test was carried out with −200# ASTM particles for two coking and two noncoking coal samples from Indian coalfields. It is observed that both the grafted products are very effective flocculants in bringing down the turbidity of supernatant liquid of coking coal fines suspension. Though they are effective flocculants in the case of noncoking coal suspension as well, the supernatant turbidity remains somewhat high. Ap-*g*-PAM performed better than St-*g*-PAM, which is distinctly apparent in the case of noncoking coal suspension. This may be ascribed to the presence of longer grafted polyacrylamide chains in case of Ap-*g*-PAM. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 2619–2625, 1998

Key words: flocculation; coal fines; amylopectin-*g*-polyacrylamide; starch-*g*-polyacrylamide

INTRODUCTION

Starch and starch-based polysaccharides exhibit some flocculation ability. But such naturally occurring polysaccharides are highly prone to biodegradation, thus lowering their shelf life and flocculation ability with time. Polyacrylamide is a water-soluble synthetic polymer exhibiting good flocculation behavior. But it is shear-degradable. It has been observed that grafting of polyacrylamide chain onto a rigid polysaccharide backbone makes the polymer less biodegradable and reasonably shear-resistant.[1] Starch consists of two types of polymers, that is, amylose and amylopec-

tin.[2,3] Amylose is essentially a linear polymer consisting of D-anhydroglucose units linked $1 \rightarrow 4$. It is the minor fraction of starch with low molecular weights ranging from 10,000 to 60,000. On the other hand, amylopectin is a highly branched polymer of D-anhydroglucose units containing $1 \rightarrow 4$ chain links with $1 \rightarrow 6$ links at branch points. It is of high molecular weight, between 50,000 and 10^6. Amylopectin is soluble in water, whereas amylose is only sparingly soluble.[4] It has been found that amylopectin-*g*-polyacrylamide (Ap-*g*-PAM) exhibits better flocculation properties in comparison with amylose-*g*-polyacrylamide (Am-*g*-PAM), which is ascribed to its high molecular weight and branched nature.[5]

Washing of coking coals has been a practice before their utilization. Of late, washing of noncoking coals for their use in thermal power

Table I   Sources of Ingredients and/or Chemicals Used

Ingredients and/or Chemicals	Source
Starch, acrylamide	E. Merck, Germany
Amylopectin	Sigma Chemicals Co., USA
Ceric ammonium nitrate	Loba Chemie, India
Acetone, hydroquinone	s.d. Fine Chemicals, India

plant and cement industry is gaining popularity. Several benefits are accrued out of beneficiation of noncoking coals, such as reduction in transportation cost, increased plant utilization factor, and reduction in specific coal consumption.[6] The washing process generates effluent containing suspended coal fines, causing environmental problems to natural water bodies like rivers. Metal ion coagulants are being used to coagulate and thereby retain the fine particles in the washery thickener. Comparatively cleaner water is released into the rivers. Metal coagulants are not very effective. Also, they are required in a large quantity. Synthetic polymers have already taken the place of metal ion coagulants as they are much more effective and are required in very small dosage, of the order of a few parts per million.

Polysaccharide-based graft copolymers have shown good flocculation quality onto iron ore[7] as well as kaolin[8] suspensions. It has been observed that starch-*g*-polyacrylamide (St-*g*-PAM) possesses higher flocculation efficiency than Am-*g*-PAM in iron ore suspension.[7] In the present work, an attempt has been made to study the flocculation characteristics of laboratory-synthesized starch-*g*-polyacrylamide and amylopectin-*g*-polyacrylamide in both coking and noncoking coal fines suspension.

EXPERIMENTAL

Materials

The sources of ingredients and chemicals used for the synthesis of graft copolymers are given in Table I. Two coking and 2 noncoking coal samples from Indian coalfields have been tested in the present work. Details of the coal sample collection and their proximate analysis results are given in Table II. Coal samples were ground to -200 mesh ASTM (that is, below 74 μm) for conducting the experiments.

Synthesis of Graft Copolymers

Synthesis of graft copolymers was carried out using a redox initiation process involving ceric ion.[9] The procedure of synthesis is briefly outlined below.[10,11]

Starch/amylopectin [1.234×10^{-2} mol in terms of anhydroglucose unit (AGU)] was dissolved in 100 cc of distilled water in a conical flask. It was heated up to 80°C and magnetically stirred. N_2 gas was purged through the solution for 30 min to drive out dissolved oxygen. Solution was cooled to 30°C. Acrylamide (0.211 mol) dissolved in 80 cc of distilled water was added to the solution. Ceric ammonium nitrate (CAN) (0.12 g) was dissolved in 50 cc of distilled water, off which 20 cc was

Table II   Location and Proximate Analysis of Coal Samples

Sample	Coal Type	Location	Proximate Analysis			
			Moisture (%)	Volatile Matter (%)	Ash (%)	Fixed Carbon (%)
C-I	Coking	Jharia 13 seam	0.9	22.3	23.4	53.4
C-II	Coking	Jharia 14 seam	1.0	24.9	17.5	56.6
NC-I	Noncoking	Talcher 2 seam	2.6	34.6	22.3	40.5
NC-II	Noncoking	Raniganj R7 seam	4.5	31.3	18.1	46.1

Table III   Details of Graft Copolymer Synthesis

Graft Copolymer	Polysaccharide (Moles of AGU)	Acrylamide (mol)	CAN (mol)	Conversion (%)	Intrinsic Viscosity [η] (dL/g)
St-g-PAM	1.234×10^{-2}	0.211	8.75×10^{-5}	85.3	6.95
Ap-g-PAM	1.234×10^{-2}	0.211	8.75×10^{-5}	79.4	8.55

added to the reaction mixture to obtain 8.75×10^{-5} mol of catalyst in the solution. N_2 gas was purged for another 30 min and stirring was continued. The reaction flask was placed in a water bath to maintain a temperature of 30°C and left for 24 h for completion of grafting. Reaction was then terminated by injecting 0.5 cc of saturated hydroquinone solution.

The grafted product was poured into excess acetone to ensure complete precipitation as well as to wash out any unreacted monomer. A milky-white grafted product was dried in a vacuum oven at 70°C for about 8–12 h to attain constant weight. It was then pulverized to −52 mesh BSS (that is, 295 μm) and packed in glass vials. Details of ingredients of the graft copolymers and their percentages of conversion are given in Table III.

Intrinsic Viscosity and IR

Viscosity was measured with the help of Ubbelohde capillary viscometer (cs/s: 0.00527). During the measurement, the temperature was maintained at 30 ± 0.1°C in water bath. From the time of flow of polymer solution (t) and that of the solvent (t_o = 160.1 s for distilled water), relative viscosity ($\eta_{rel} = t/t_o$) was obtained. Specific viscosity was calculated from the relationship $\eta_{sp} = (t - t_o)/t_o = \eta_{rel} - 1$. Knowing the concentration of the polymer solution (C) in g per decilitre (g/dL), reduced viscosity ($\eta_{red} = \eta_{sp}/C$), and inherent viscosity ($\eta_{inh} = \ln \eta_{rel}/C$) were calculated for a set of 5 polymer concentrations. Intrinsic viscosity [η] was then obtained from the common ordinate intercept on extrapolation of plots of reduced viscosity versus concentration and inherent viscosity versus concentration.[12,13] Intrinsic viscosity results have been shown in Table III as well.

Infrared (IR) spectra were recorded using a Perkin–Elmer 630 IR spectrophotometer in solid state using a potassium bromide (KBr) dispersion method in the transmittance mode. A uniform resolution of 3.2 cm^{-1} was maintained in all cases.

Flocculation Jar Test

Flocculation tests of coal fines suspension were carried out on standard flocculation jar apparatus (supplied by M.B. Instruments, Bombay, India). The flocculation procedure was followed in the line of Bratby[14] with minor modifications. The apparatus consists of 6 stirrer blades connected to a variable speed motor through a gear system. In 1-L beakers, 400 cc of 1 wt % coal suspension was taken. The beakers were placed on the flocculator dipping the stirrer blades in the suspension. Under a low stirring condition, the polymer solution was added to each beaker to make predetermined polymer dosage (0.25 to 10 ppm with respect to suspension volume). Immediately after the addition of polymer solution, the suspensions were stirred at a constant speed of 75 rpm for 2 min, followed by low stirring at 25 rpm for 5 min. The flocs were allowed to settle down for 15–20 min. Clean supernatant liquid was drawn from a depth of 1 cm, and its turbidity was measured using a digital nephelo turbidity meter (supplied by Systronics, Ahmedabad, India) to express the turbidity in nephelometric turbidity unit (NTU).

RESULTS AND DISCUSSION

It is an established fact that the redox-initiated process of graft copolymerization onto the polysaccharide backbone generates free radicals on the polysaccharide backbone[15] itself, leaving little scope for homopolymer formation,[16] if at all. Studies on homopolymerization by Owen and Shen[17] indicate that a monomer concentration of less than 2.0M and a ceric ammonium nitrate concentration of less than 0.1M did not result in homopolymerization. Hence, in the present synthesis of polyacrylamide onto starch–amylopectin, the ceric-ion induced redox initiation method has been adopted. To avoid formation of homopolymer, concentrations of acrylamide and ceric ammonium nitrate were kept lower than their

Figure 1 Infrared spectra of amylopectin, polyacrylamide, and Ap-*g*-PAM.

above-mentioned critical concentrations. The percentage of conversion of graft copolymer (Table III) was calculated using the following relation[18]:
% conversion = [(weight of graft copolymer − weight of polysaccharide)/weight of acrylamide] × 100. The percentage of conversion of Ap-*g*-PAM (85.3%) was slightly higher than that for St-*g*-PAM (79.4%). Assuming that no homopolymerization took place, as observed by Owen and Shen,[17] the polyacrylamide chains are slightly longer in case of Ap-*g*-PAM.

IR spectra of amylopectin, polyacrylamide, and Ap-*g*-PAM have been shown in Figure 1. The characteristic absorption due to >C=O group, which is present in polyacrylamide, is absent in amylopectin. A strong absorption characteristic of >C=O in Ap-*g*-PAM is thus a proof of grafting.

Viscosity of a polymer solution is considerably higher than that of the solvent. Viscosity of the polymer solution is a function of the hydrodynamic volume of the polymer in solution which, in turn, depends on the molecular weight of the polymer, its structure, the nature of solvent, as well as the solution temperature.[19] Keeping the type of solvent and experimental temperature fixed, intrinsic viscosity values can be used to estimate the molecular weight. Intrinsic viscosity[8] is lower for the branched polymer compared to a linear polymer of approximately similar molecular weight. Again, the longer the chain in a graft

Figure 2 Determination of intrinsic viscosity $[\eta]$: (a) St-*g*-PAM; (b) Ap-*g*-PAM.

copolymer, the higher the intrinsic viscosity. In this study, intrinsic viscosity was graphically calculated from the reduced and inherent viscosity (Fig. 2). Intrinsic viscosity of Ap-*g*-PAM and St-*g*-PAM was 8.55 and 6.95, respectively. The higher intrinsic viscosity of Ap-*g*-PAM is due to the longer polyacrylamide chain, as observed from the percentage conversion values.

Viscosity of polymer solution is also important in the process of flocculation. For effective flocculation, the polymer should be dispersed uniformly in the colloidal suspension. Hence, it is desired that the concentration of flocculant solution should be very low at the time of mixing so that the polymer solution is uniformly dispersed. In the present experiments, the concentration of the aqueous solution of the flocculants is kept very low, at 10^{-4} g/cc. And since the coal powder has

been uniformly suspended in the water by stirring, it is expected that the polymer is also uniformly dispersed in the bulk of the suspension.

In the flocculation jar test, turbidity value of supernatant liquid has been taken as the measure of flocculation efficacy of polymer. Plots of supernatant turbidity versus polymer dosage for the coking and noncoking coals are given in Figures 3 and 4, respectively. The figures show that there is no substantial difference in the flocculation ability of St-*g*-PAM and Ap-*g*-PAM on the 2 coking coal (C-I and C-II) fines suspension. But there is marked difference in their performance on the noncoking coals (NC-I and NC-II). Coking and noncoking coal suspensions behave widely different as far as turbidity is concerned. For 1 wt % suspension, without addition of polymer in jar test, turbidity of coking coals was in the range of 10–20 NTU, while that for noncoking ones was in the range of 600–1000 NTU. The optimum dosage of the grafted products was found to be 1–2 ppm for coking coals and 2–3 ppm for the noncoking coals. In the optimum dosage range, turbidity of both noncoking coals was around 75 NTU with St-*g*-PAM and around 20 NTU with Ap-*g*-PAM. Thus, it is obvious that Ap-*g*-PAM performs better than St-*g*-PAM as far as noncoking coal suspension is concerned.

Figure 3 Effect of polymer dosage on turbidity for coking coals: (a) coal C-I; (b) coal C-II.

Figure 4 Effect of polymer dosage on turbidity for noncoking coals: (a) coal NC-I; (b) coal NC-II.

There are 2 main predominant mechanisms involving polymeric flocculation: electrostatic patch mechanism and bridging mechanism.[14,20] In electrostatic patch mechanism, polyelectrolytes carrying high charge density get adsorbed on charged colloidal particles, leaving some charged patches on them. Such oppositely charged patches of different particles attract each other to form flocs. On the other hand, the bridging mechanism involves binding or bridging individual particles by way of adsorption of polymeric flocculant on them to form flocs. Here, charge of the particles and/or polymer does not play any significant role in the present study, and the graft copolymers St-*g*-PAM and Ap-*g*-PAM are nonionic in nature. Hence, expectedly, the flocculation process is dominated by bridging mechanism. The better efficiency of Ap-*g*-PAM on noncoking coal suspension may be explained through the higher molecular weight and longer polyacrylamide chains on the rigid and branched amylopectin backbone, as pointed out by Singh.[5] In the flocculation process by grafted polysaccharides, the dangling branches of flexible polyacrylamide will have easier approachability. As the superna-

tant liquid for coking coal under optimum polymer dosage was nearly turbidity free, superiority of Ap-*g*-PAM over St-*g*-PAM could not be observed. However, at dosages lower than the optimum ones, Ap-*g*-PAM exhibited better performance than St-*g*-PAM.

CONCLUSION

The study shows that laboratory synthesized graft copolymers, Ap-*g*-PAM and St-*g*-PAM, can efficiently flocculate both coking and noncoking coal suspensions. Higher percentage conversion and intrinsic viscosity of Ap-*g*-PAM imply that it has got longer branch chains of polyacrylamide compared to St-*g*-PAM. Though superiority of Ap-*g*-PAM over St-*g*-PAM is noticed only in lower ranges for coking coal suspension, it is highly reflected over the wide range of dosage (0.25–10 ppm) in the case of noncoking coal suspension.

The optimum dosage for both the graft copolymers is 1–2 ppm for coking coal and 2–3 ppm for noncoking coal suspension. At their optimum dosage, the supernatant liquid of coking coal suspension become almost turbidity-free. Though, in the case of noncoking coal suspension, turbidity is lowered down to a great extent, it still remains considerably high.

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