The Flocculation and Rheological Characteristics of Hydrolyzed and Unhydrolyzed Grafted Sodium Alginate in Aqueous Solutions

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ABSTRACT: Sodium alginate is a natural anionic polysaccharide obtained from natural and microbial resources. It is also used as a flocculating agent and thickener. It is grafted with polyacrylamide, in the presence of ceric ammonium nitrate (CAN) as an initiator. The graft copolymer (SAG-g-PAM) is again hydrolyzed with some amount of alkali. The flocculation characteristics of hydrolyzed graft copolymer (Hyd SAG-g-PAM) are compared with that of the unhydrolyzed ones, in 5 wt % kaolin and 10 wt % iron ore suspensions. The flocculation characteristics of the hydrolyzed graft copolymer are also compared with those of some of the commercial flocculants. The SAG-g-PAM and Hyd SAG-g-PAM are characterized by IR and intrinsic viscosity measurements. The rheological properties of aqueous solutions of hydrolyzed and unhydrolyzed graft copolymers are measured by Advanced AR-1000 Rheometer. There is drastic enhancement in flocculation and viscosifying characteristics on hydrolysis of the graft copolymers. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 1480–1488, 2004

Key words: graft copolymer; hydrolyzed graft copolymer; intrinsic viscosity; flocculation; shear rate; rheology

INTRODUCTION

Although water-soluble synthetic polymers find wide application as flocculating agents, the potential problems associated with their use are lack of biodegradability and high cost. On the contrary, natural polymers (mainly polysaccharides) are fairly shear stable and biodegradable.[1] The biodegradability of natural polymers reduces their shelf life. Grafting of the synthetic polymers onto the polysaccharides backbone introduces versatile properties in the copolymer due to the drastic change in the original structure. The graft copolymers are very efficient and shear stable flocculants.[2] They have well-controlled biodegradability. Various types of graft copolymers have been synthesized by grafting polyacrylamide onto the polysaccharides (starch,[3] amylopectin,[4] guar gum,[5] hydroxypropyl guar gum,[6] sodium alginate,[7] and psyllium[8]) backbone. On grafting the synthetic polymer polyacrylamide (PAM) onto the polysaccharide backbone, the flocculation as well as viscosifying characteristics of the graft copolymer are increased.[4,7] This is due to the ease of approachability of the dangling grafted polyacrylamide chains to the contaminants in the effluents.[9]

Sodium alginate is a sodium salt of alginic acid, and it is a water-soluble anionic polymer. Alginates are hydrophilic polysaccharides found in brown seaweeds, comprising up to 40 wt % of the dry matter. Sodium alginates are well known for their ability to form a gel in contact with most of divalent cations, and this property has been widely used in the food and beverage industry, as well as in the pharmaceutical sector. Alginates are either homopolymers of D-mannuronic acid or L- guluronic acid. Alginates are also linear unbranched copolymers of two uronic acids, containing β- (1→4)-linked D-mannuronic acid (M) and α- (1→4)-linked L-guluronic acid (G) residues.[10]

Sodium alginate itself is used as a flocculating agent. On purification and grafting the sodium alginate, the flocculation characteristics increase severalfold.[11] The grafted sodium alginate also acts as a good flocculating agent for coal mine suspensions.[12] Among all the graft copolymers, those having fewer but longer polyacrylamide chains show better performance than the others.[9] We synthesized SAG-g-PAM graft copolymer by grafting SAG with polyacrylamide by using ceric ammonium nitrate (CAN) as initiator. The polyacrylamide chains are grafted onto the sodium alginate backbone by a ring opening mechanism.[13–16]

Viscosity is an important characteristic's for all the fluid materials, especially of polymer solutions. For polymers, it is used as a measuring stick. The viscosity

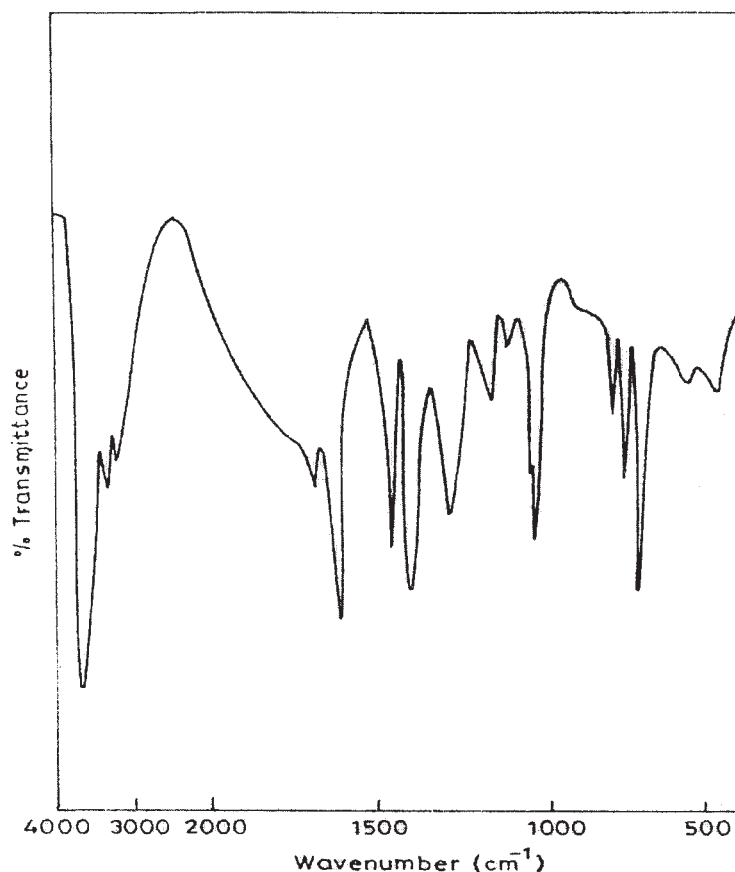*Correspondence to:* R. P. Singh (rps@matsc.iitkgp.ernet.in or rpsiitkgp@yahoo.com).

Figure 1   IR spectra of Hyd SAG-g-PAM.

of aqueous solutions of polymers is built through the entanglement of the random polymer coils. The viscosity of a polymer solution depends on concentration, temperature, solvent quality, polymer chain architecture, and molecular weight of the polymer. It has been observed that on hydrolysis of the graft copolymer with a certain amount of alkali, the flocculation characteristics increase tremendously.[17] Recently it has been observed that the viscosity of aqueous solutions of hydrolyzed graft copolymers increases several hundred times that of the unhydrolyzed graft copolymer.[18] The present article reports the synthesis of unhydrolyzed and hydrolyzed graft copolymers. It also reports the details of their rheological investigations and flocculation performance in various suspensions.

EXPERIMENTAL

Materials

Sodium alginate was procured from Aldrich Chemical Company, Milwaukee, WI, USA. Acrylamide (for synthesis) was procured from E. Merck, Hohenbrunn, Germany. CAN was obtained from Loba Chemie, Mumbai, India. Acetone and hydroquinone were pro-

cured from S. D Fine Chemicals, Mumbai, India. Kaolin was procured from B. D Pharmaceutical, Howrah, India. Iron ore was a gift from Kiriburu iron ore mines, Jharkhand, India. Potassium hydroxide (analar) was procured from E. Merck, Mumbai, India.

Synthesis of SAG-g-PAM

The graft copolymer was synthesized by using CAN as initiator. The whole grafting reaction was carried out in nitrogen atmosphere, as oxygen inhibits the polymerization of vinyl monomers.

The detailed synthetic procedure is described elsewhere.[11]

Synthesis of Hyd SAG-g-PAM

Alkaline hydrolysis of SAG-g-PAM was performed as follows: First, 2 g of SAG-g-PAM was dissolved in 200 cc of distilled water to make a clear solution. Then 25 cc of 1(M) KOH was added to it. The whole solution was placed in a thermostatic water bath at 50°C. After one hour, the contents of the flask were poured into 400 mL of ethyl alcohol. The product was precipitated with excess of alcohol. It was then dried.

TABLE I
Intrinsic Viscosity Values of SAG, SAG-g-PAM, and Hyd SAG-g-PAM

Polymer	Intrinsic viscosity (dl/g)
SAG	18.9
SAG-g-PAM	21
Hyd SAG-g-PAM	66.92

Infrared spectroscopy

A Perkin–Elmer 630 IR spectrophotometer was used to record the IR spectra in the range of $4000-400\ cm^{-1}$. The IR spectra of the polymer samples were recorded in the solid state using the KBr pellet method.

Viscosity measurement

For the measurement of intrinsic viscosity of the polymers, 0.125 g each of SAG, SAG-g-PAM, and Hyd SAG-g-PAM were dissolved in 100 mL of distilled water slowly to avoid lumping. Intrinsic viscosity measurements were carried out with the help of an Ubbelohde viscometer with constant (0.003867) at 28 $\pm$ 0.1°C at various dilutions. For the measurement of

absolute viscosity, 0.5 g/dL of aqueous solutions of SAG and SAG-g-PAM were prepared. It was very difficult to prepare 0.5 g/dL of Hyd SAG-g-PAM solution, because at this concentration gels are formed instead of clear solution. So, we measured the absolute viscosity of Hyd SAG-g-PAM at 0.2 g/dL concentration.

The time-of-flow for solutions was measured at five different concentrations. From the time-of-flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), the relative viscosity ($\eta_{rel} = t/t_0$) was obtained. The specific viscosity was calculated from the relationship $\eta_{sp} = \eta_{rel}-1$. The reduced viscosity, η_{red} (η_{sp}/C), and the inherent viscosity, η_{inh} (ln η_{rel} /C), were than calculated, where C is the polymer concentration in g/dL. The intrinsic viscosity is evaluated as the point of intersection after extrapolation[19] of the two plots, η_{sp}/C versus C and (ln η_{rel} /C) versus C, to zero concentration.

Rheological studies

The rheological study of aqueous solutions of SAG, SAG-g-PAM, and Hyd SAG-g-PAM was carried out in controlled stress AR-1000 Advanced Rheometer. For
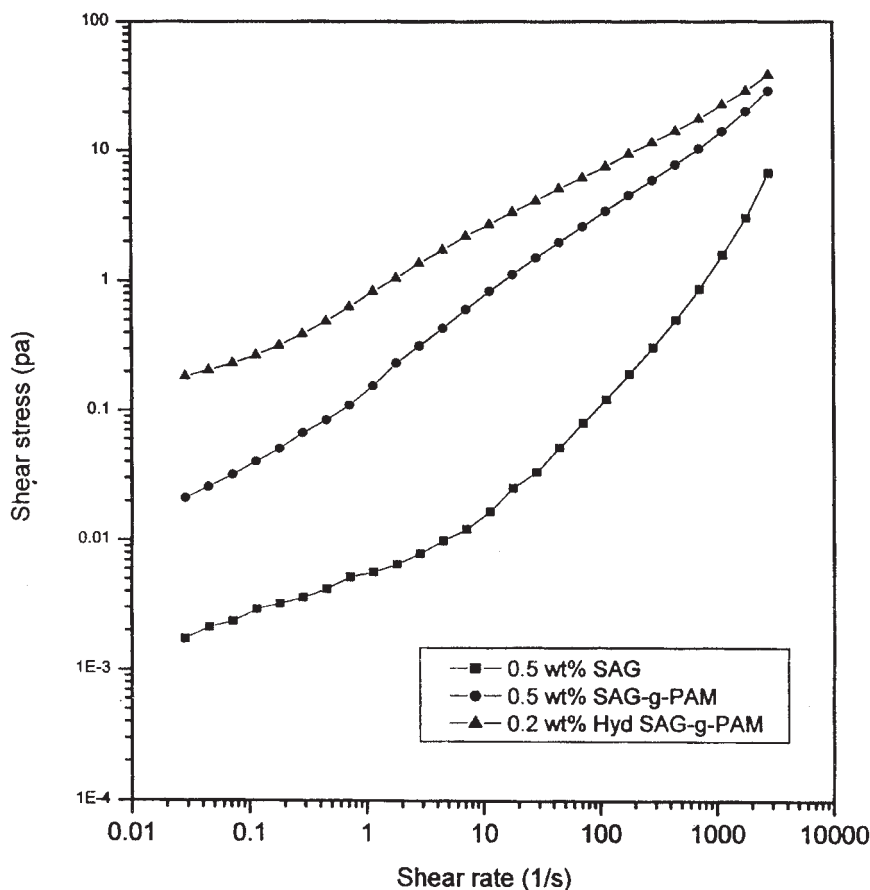

Figure 2 Shear stress versus shear rate of SAG, SAG-g-PAM solutions, and Hyd SAG-g-PAM.
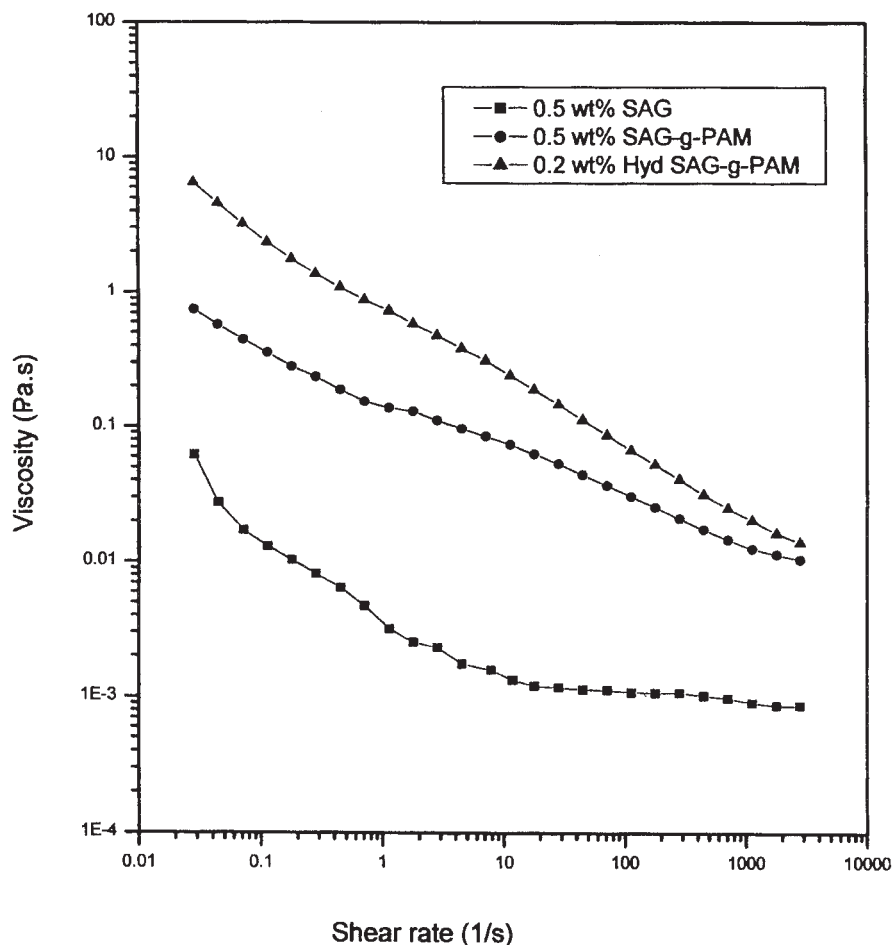
Figure 3 Viscosity curves of SAG, SAG-g-PAM, and Hyd SAG-g-PAM solutions.

this study, we used a 2-degree cone of diameter 4 cm and with truncation of 46 micron. The temperature of the system was maintained at 30°C throughout the experiment. All the measurements are based on the assigned shear rate in CR (controlled rate) mode ranging from 0.028 to 2800 s^{-1}. The rheological study of SAG and SAG-g-PAM was carried out in 0.5 wt % solutions and that of Hyd SAG-g-PAM was in 0.2 wt % solution. We measured two parameters, namely, shear stress and shear viscosities, of the aqueous solution of the polymer samples versus shear rate.

Flocculation study

The flocculation characteristics of SAG, SAG-g-PAM, Hyd SAG-g-PAM, and some commercial flocculants were measured by the column settling method. The flocculation studies were carried out in 5 wt % kaolin and 10 wt % iron ore suspension with the help of a 100 mL stoppered graduated cylinder.

This test employs a 100 mL stoppered graduated cylinder and stopwatch. First of all, the slurry sample was taken in the cylinder and then polymer solution was added into it. The cylinder was inverted 10 times for thorough mixing. After the cylinder was set upright, the height of interface between water and settling solid bed was measured over time interval.

RESULTS AND DISCUSSION

Synthesis of SAG-g-PAM and Hyd SAG-g-PAM

The graft copolymer SAG-g-PAM was synthesized by grafting PAM chains onto the SAG backbone by a free radical polymerization technique using CAN as initiator. In this reaction the ceric ion first involves the formation of a chelate complex, which decomposes to generate free radical sites on the SAG backbone.[13,14] These active sites in the presence of acrylamide monomers generate graft copolymers. The possibility of homopolymerization is remote as the monomer and ceric ammonium ion concentration are kept below $2.0M$ and $0.1M$, respectively (within the limits of Owen and Shen[20]). However, an insignificant homopolymerization of acrylamide monomers takes place. After that, the homopolymer polyacrylamide
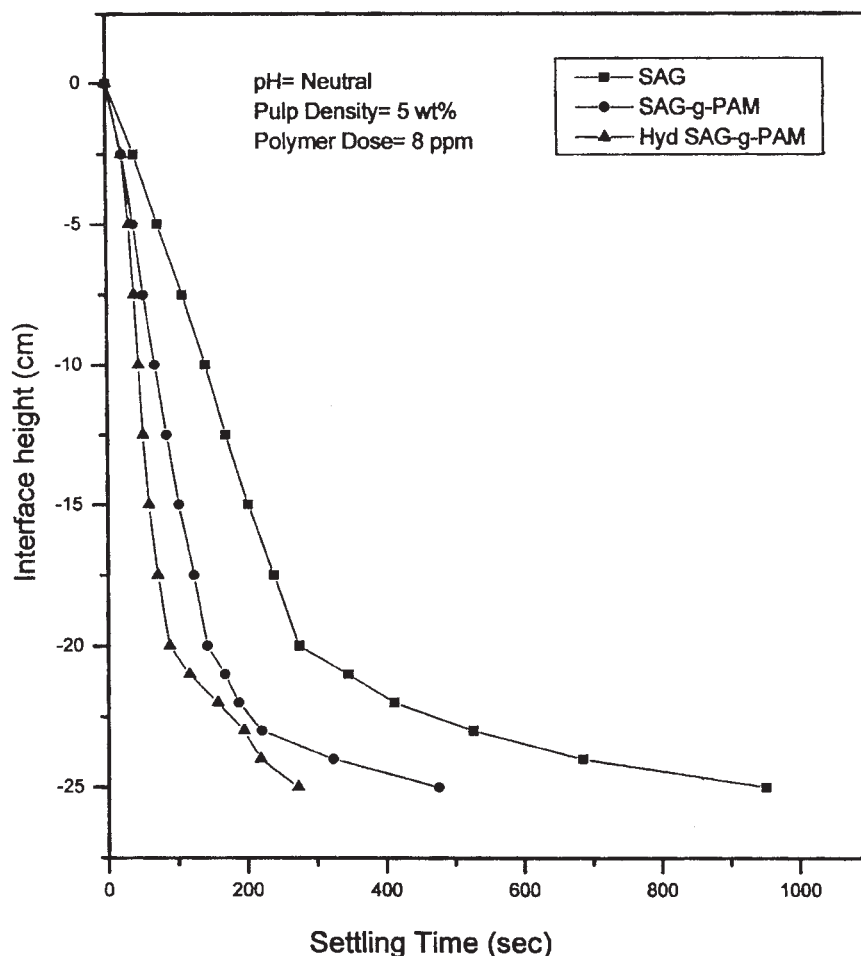
Figure 4 Comparison of flocculation efficiency of SAG, SAG-g-PAM, and Hyd SAG-g-PAM in 5 m % kaolin suspension.

was removed by using a formamide and acetic acid (1 : 1 by volume) mixture.[21]

The above graft copolymer, SAG-g-PAM, was then hydrolyzed with a certain amount of KOH solution, the aim being to straighten and expand the flexible polyacrylamide chains. During alkaline hydrolysis of SAG-g-PAM with alkali, two reactions are expected to occur: (1) saponofication reaction of amide groups to carboxyl groups, and (2) deetherification of the polysaccharide and depolymerization reaction of the polyacrylate component of the graft copolymer.[22] Khalil et al.[23] observed that during alkaline hydrolysis of polyacrylamide-starch graft copolymer, by using alkali up to a concentration of 1(N) and temperature up to 80–90°C, only the saponification reaction occurs. As in the present case, the hydrolysis reaction was carried out below the above-mentioned reaction conditions; the only reaction is saponification. The carboxyl content depends on the concentration of alkali, and the duration and temperature of the treatment.

IR spectroscopy

The grafting and hydrolysis are supported by IR spectroscopy. The proof of grafting in SAG-g-PAM is de-

scribed elsewhere.[24] Figure 1 shows the IR spectra of Hyd SAG-g-PAM. The peaks, which were present in the IR spectra of SAG-g-PAM, are also present in the IR spectra of Hyd SAG-g-PAM but at slightly different frequencies and absorbance. The intensities of the peaks at 3300 and 3100 cm^{-1} are decreased, because some amide groups are converted to the acid groups. The presence of a broad peak at around 1613 cm^{-1} and 1402 cm^{-1} is due to the symmetrical and asymmetrical stretching of the COO^- ion. The peak at 1436 cm^{-1} is due to the –OH stretching of the carboxylic acid group. The broad peak at around 1308 cm^{-1} is due to the –C-O stretching of the carboxylic acid group. The presence of the above bands in the IR spectra of Hyd SAG-g-PAM is proof of hydrolysis of our graft copolymer.

Viscosity measurement

The intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which, in turn, depends upon its molecular weight, structure, nature of the solvent and temperature of the medium. The hydrodynamic volume of SAG-g-PAM is more than the hydrodynamic volume of SAG, be-
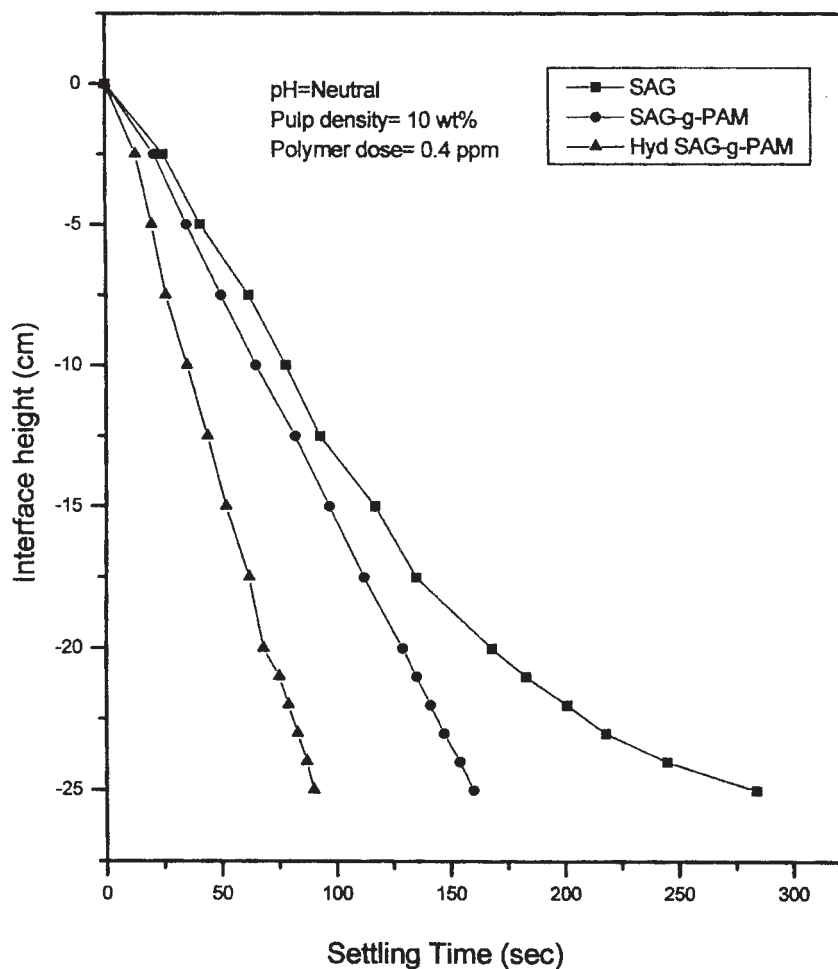
Figure 5 Comparison of flocculation efficiency of SAG, SAG-g-PAM, and Hyd SAG-g-PAM in 10 wt % iron ore suspension.

cause of the presence of the longer dangling grafted PAM chains. So the intrinsic viscosity of SAG-g-PAM is more than the SAG, which is also observed in practice. On hydrolysis, the –CONH$_2$ groups of the graft copolymer were converted to –COO$^-$ groups. The chains become straightened by repulsion of adjacent negatively charged groups. Therefore, the hydrodynamic volume increases and so does the intrinsic viscosity value. The intrinsic viscosity values of SAG, SAG-g-PAM, and Hyd SAG-g-PAM are given in Table I.

Rheological studies

In a steady state shear flow test, two main relationships, that is, the flow behavior curve (Fig. 2) and the viscosity curve (Fig. 3) of double logarithmic scales illustrate the rheological fingerprints of the sample under study. The double logarithmic plots of shear stress versus shear stress are plotted in Figure 2. From Figure 2 it is observed that all the polymer solutions show non-Newtonian behavior.

With increases in shear rate, the shear stress increases.

Figure 4 shows the viscosity curves of the polymer solutions. Here we also plotted the log-log plot of viscosity versus shear rate of aqueous solutions of SAG, SAG-g-PAM, and Hyd SAG-g-PAM at a constant temperature of 30°C. With increases in shear rate, the viscosity of SAG, SAG-g-PAM, and Hyd SAG-g-PAM solutions decreases, which is a strong proof of the shear thinning behavior of our polymer samples. At low and high shear rates, the viscosity of Hyd SAG-g-PAM solutions is found to be more than the viscosity of SAG-g-PAM graft copolymer and the SAG solution. This is because of the presence of longer chains in Hyd SAG-g-PAM, than those of the corresponding graft copolymer. On hydrolysis, the amide groups of the PAM chains in the SAG-g-PAM graft copolymer are converted to the corresponding COO$^-$ [1] groups. The presence of two negative groups on adjacent carbon atoms repel each other, and the chains become straightened. At high shear rate, the entanglements of the grafted chain break up and the viscosity decreases.
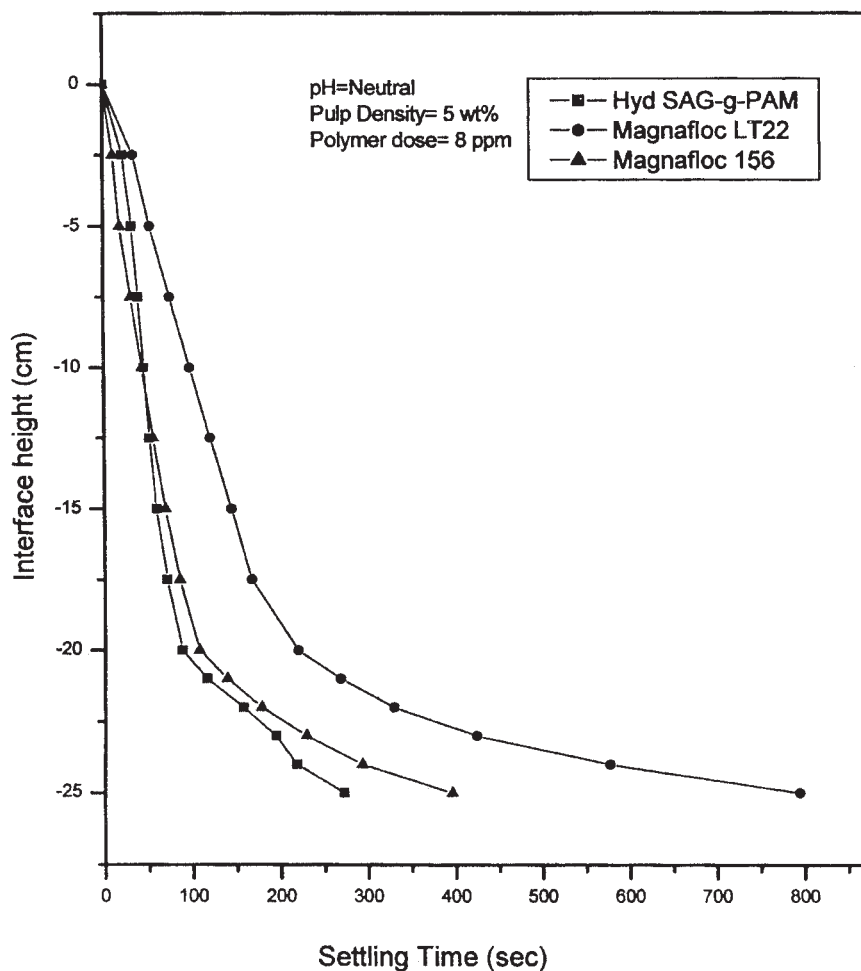
Figure 6 Comparison of flocculation efficiency of some commercial flocculants and Hyd SAG-g-PAM in 5 wt % kaolin suspension.
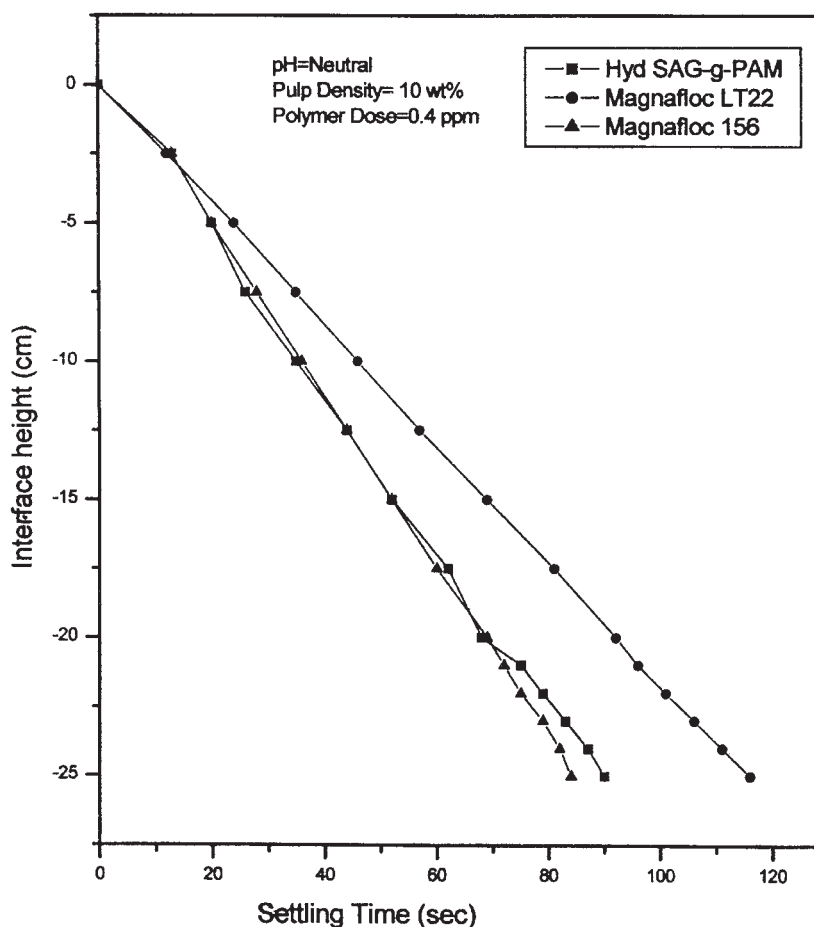
Flocculation study

The flocculation performance of SAG, SAG-g-PAM, Hyd SAG-g-PAM, and some commercial flocculants were compared in kaolin and iron ore suspensions. The flocculation performance in two different suspensions has been studied at various concentrations and pulp densities for distinct observation. We plotted the height of interface between the solid and liquid against the settling time. It is apparent from Figure 4 that SAG-g-PAM shows better performance than SAG itself in kaolin suspension. This is because of the easy approachability of the dangling grafted chain of PAM to the contaminants as per Singh's model.[9]

Among the hydrolyzed and unhydrolyzed graft copolymers, the Hyd SAG-g-PAM shows better performance than the unhydrolyzed graft copolymer. On hydrolysis, the $-CONH_2$ groups of the graft copolymer were converted to $-COO^-$ groups. The presence of the two negative groups on the adjacent carbon atoms repel each other; as a result, the chain becomes straightened to some extent. As the chain becomes

straightened, it still has flexibility and hence the approachability becomes higher to the contaminant particles.

Hyd SAG-g-PAM shows better performance when the flocculation study was carried out in 10 wt % iron ore suspension. Figure 5 shows the comparison of the flocculation efficiency of hydrolyzed and unhydrolyzed graft copolymers in iron ore suspension.

The major mechanism of flocculation by polymers is bridging.[25] The bridging takes place by adsorption of a polymer molecule at more than one site on a particle or at sites on different particles. When the long chain polymer molecules are adsorbed on the surface of particles, they tend to form loops and extend some distance from the particle surface into the aqueous phase. Their ends also dangle and get adsorbed on the surface of another particle, forming a bridge between the particles. For effective bridging to occur, the length of polymer chains should be long so that they can extend from one particle surface to another.

Figure 7 Comparison of the flocculation efficiency of commercial flocculants and Hyd SAG-g-PAM in 10 wt % iron ore suspension.

The flocculation performance of the Hyd SAG-g-PAM is again compared with some commercial flocculants (Magnafloc LT 22 and Magnafloc 156) available in the international market. The commercial flocculants are PAM based linear polymers. Figures 6 and 7 show the comparison of the flocculation efficiency of Hyd SAG-g-PAM and the commercial flocculants in kaolin and iron ore suspension, respectively. In kaolin suspension, at first Magnafloc 156 settles faster than Hyd SAG-g-PAM and Magnafloc LT 22. However, with increase in the interface height, the settling rate of Magnafloc 156 decreases and that of Hyd SAG-g-PAM increases. Overall, Hyd SAG-g-PAM shows better performance than the two commercial flocculants in kaolin suspension. In iron ore suspension, at first Hyd SAG-g-PAM and Magnafloc 156 show similar performance, but Magnafloc 156 settles slightly faster. The better flocculating power of the hydrolyzed graft copolymer over the linear polymers is the result of effective bridging, as already discussed. In the case of hydrolyzed and unhydrolyzed graft copolymers, the approachability of the dangling grafted chains to the contaminants are more, and they can easily bind the colloidal particles through bridging and form flocs.

CONCLUSION

The synthesized SAG-g-PAM graft copolymer performs as an efficient flocculating agent. Again, on hydrolysis, the flocculation and viscosifying characteristics of the graft copolymer increase. The Hyd SAG-g-PAM graft copolymer shows better performance than the commercial flocculants. The viscosity of aqueous solution of Hyd SAG-g-PAM is found to be much more than that of the graft copolymer SAG-g-PAM and SAG solutions.

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