

Development of Graft Copolymer Flocculating Agents Based on Hydroxypropyl Guar Gum and Acrylamide

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ABSTRACT: Graft copolymers of hydroxypropyl guar gum (HPG) with polyacrylamide (PAM) have been synthesized using a ceric ion-induced solution polymerization technique at 28°C. Six graft copolymers have been synthesized with variation in the number and length of grafted PAM chains. The graft copolymers were characterized by viscometry, infrared (IR) spectroscopy, and thermal analysis studies. Flocculation jar tests were carried out in 0.25 wt % kaolin, iron ore, and silica suspensions. Among the series of graft copolymers, the one with fewest but longest PAM chains shows the better performance. The flocculation characteristics of this best performing graft copolymer are compared with various commercially available flocculants in the three suspensions. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1776–1785, 2001

Key words: hydroxypropyl guar gum; polyacrylamide; graft copolymers; flocculation

INTRODUCTION

Flocculation is a process of bringing together smaller particles to form large particles, often highly porous in nature.¹ Flocculation of suspensions is brought about by addition of minute quantity of chemicals known as flocculants of various characteristics. The principal practical applications of flocculation are in raw and waste water clarification, sludge dewatering, mineral processing, etc.^{1–4} The flocculants being used are broadly divided into two categories, i.e., inorganic and organic. The inorganic flocculants most often used are based on the hydrolyzable salts of aluminum and iron.¹ The organic flocculants are further divided into two categories: synthetic and natural. Synthetic flocculants are available in all three forms, i.e., cationic, anionic, and nonionic, which include polyacrylamide (PAM), polyacrylic acid,

poly(diallyl dimethyl ammonium chloride) (DADMAC), and polystyrene sulfonic acid. By contrast, starch, cellulose, alginic acid, guar gum, and so forth, are natural polymers used as flocculants. Some of the natural polymers also bear ionic groups.

The extensive use of polymers as flocculants is attributable to their distinct characteristic attributes.⁵ The polymers are convenient to use and do not affect the pH value of the medium. They are used in minute quantities (1–5 ppm) and the flocs formed during flocculation are larger, stronger, and better settling than the simple coagulating electrolytes. Large tonnage use of inorganic flocculants produces a lot of sludge, which is hardly a problem in the case of polymeric flocculants. Among the polymeric flocculants, the synthetic polymers can be tailor-made by controlling the molecular weight, molecular weight distribution, chemical structure of polymers, nature and ratio of functional groups on polymeric backbone. Thus, as a result of versatile tailorability, synthetic polymers are very efficient flocculants. However, a great advantage of natural polymers

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over synthetic ones is because of their biodegradability, nontoxicity, and shear resistant characteristics. The advantage of natural polymers, i.e., their biodegradability, comes as a major drawback, as it reduces their storage life and efficiency towards flocculation and drag reduction due to lowering of molecular weight. In the past, many attempts have been made to combine the best properties of both by grafting synthetic polymers onto natural ones.^{6,7} It has been observed that grafting of PAM chains onto a rigid polysaccharide backbone makes the polymer less biodegradable and reasonably shear-resistant.⁸ Polysaccharide-based graft copolymers have shown better flocculation performance with kaolin,⁹ as well as iron ore¹⁰ suspensions. Further, by variation in the number and length of grafted PAM chains onto the polysaccharide backbone, it has been found that the graft copolymers with fewer but longer PAM chains are more efficient drag reducing and flocculating agents.^{7,11,12}

It was proposed by one of the authors (R.P.S.)⁷ that graft copolymers are much more efficient than the linear polymers because of their greater "approachability" to the contaminants, which could be the result of the spreading effect of the dangling grafted PAM chains on the rigid polysaccharide backbone.^{7,13,14} Among the grafted guar gum, xanthan gum, carboxymethyl cellulose, sodium alginate, and starch, it has been found that grafted starch is the most efficient flocculant.⁷ Starch consists of linear amylose and amylopectin. Hence, amylose and amylopectin were grafted with PAM chains. Among all the polysaccharides, grafted amylopectin^{9,15,16} has been found to have best flocculation efficiency giving credence to the proposed model.⁷ Some of the effects have been studied by grafting PAM onto guar gum.^{7,13} Flocculation characteristic of PAM-grafted hydroxypropyl guar gum (HPG) has not been reported so far. Many rheological investigations have been carried out on HPG¹⁷ because of its wide application in oil field operations. In the present study, PAM branches grafted onto HPG and their flocculation efficiency compared with some of the commercially available flocculants.

EXPERIMENTAL

Materials

HPG was procured from Shell (U.K.). HPG is a derivatized form of guar gum (GG). The degree of

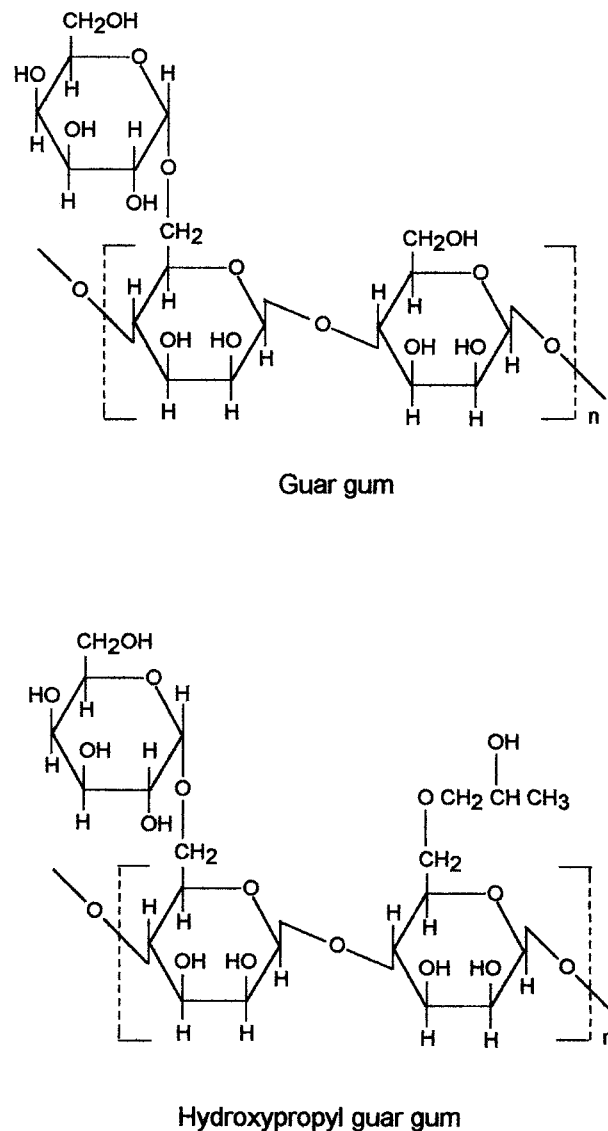


Figure 1 Structure of guar gum (GG) and hydroxypropyl guar gum (HPG).

substitution by the hydroxypropyl group is 0.5.¹⁷ Guar gum is a naturally occurring polysaccharide, which is composed of (1-4)- β -linked D-mannose units with (1-5)- α -linked D-galactose units randomly attached as side-chains.¹⁸ The structures of GG and HPG are shown in Figure 1. Acrylamide and ceric ammonium nitrate (CAN) were purchased from Loba Chemie (Mumbai, India). Acetone and hydroquinone were supplied by S.D. Fine Chemicals (Mumbai, India). Sodium nitrate was supplied by E. Merck (Mumbai, India). Five commercial flocculants, namely, Magnafloc LT 22, Magnafloc 156, Magnafloc 351, Rishfloc 440 HV, and Rishfloc 226 LV were used for com-

Table I Details of the Sources and Chemical Nature of the Commercial Flocculants

Flocculant	Source	Chemical Nature
Magnafloc LT 22	Allied Colloids, England	Cationic
Magnafloc 156	Allied Colloids, England	Anionic
Magnafloc 351	Allied Colloids, England	Non-ionic
Rishfloc 440 HV	Rishabh Chemicals Pvt. Ltd., India	Anionic
Rishfloc 226 LV	Rishabh Chemicals Pvt. Ltd., India	Non-ionic

parison. The sources of commercial flocculants along with their chemical nature are given in Table I. All the commercial flocculants are PAM-based linear polymers. However, their detailed specifications are not known. Kaolin was supplied by C.D. Pharmaceutical works (Howrah, India). Iron ore was obtained from Joda Mines (Bihar, India). Silica was procured from Jyoti Chemicals (Howrah, India). HPG was used after extraction with 95% ethyl alcohol for 70 h. All other chemicals were used without further purification.

Synthesis

The graft copolymers were synthesized by ceric ion-induced redox initiation method.^{19,20} The synthetic parameters are summarized in Table II. The graft copolymers were treated with a mixture of formamide and acetic acid (1:1 by volume) to remove the homopolymer polyacrylamide.²¹ The details of the synthetic procedure and extraction scheme are given in our previous article.²²

Viscosity Measurements

Viscosity measurements on the polymer solutions were carried out with a Ubbelohde viscometer (CS/S: 0.00575) at $27 \pm 0.1^\circ\text{C}$. The viscosities

were measured in 1M NaNO₃ solution. 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), relative viscosity ($\eta_{\text{rel}} = t/t_0$) was obtained. Specific viscosity was calculated from the relation $\eta_{\text{sp}} = \eta_{\text{rel}} - 1$. Then, the reduced viscosity (η_{sp}/C), and the inherent viscosity ($\ln \eta_{\text{rel}}/C$) were calculated, where C is the polymer concentration in g/dL. The intrinsic viscosity was obtained (from the point of intersection) after extrapolation²³ of two plots, i.e., η_{sp}/C versus C , and ($\ln \eta_{\text{rel}}/C$) versus C , to zero concentration (as shown in Fig. 2). The intrinsic viscosity values of all the graft copolymers are reported in Table II.

Infrared Spectroscopy

A Perkin-Elmer 630 IR spectrophotometer was used to record the IR spectra within the range of 4000–400 cm⁻¹. The IR spectra of HPG, PAM, and HPG-grafted PAM (HPG-g-PAM 6) were recorded in solid state using a KBr pellet method.

Thermal Analysis

The thermogravimetric analysis of HPG, PAM, and HPG-g-PAM 6 was carried out with a Stanton

Table II Synthetic Details of the Graft Copolymers

Sl. No.	Polymer	Moles of MSU ^a	Acrylamide (mol)	Amount of CAN (mmol)	Conversion ^b (%)	Intrinsic Viscosity (dL/g)
I	HPG-g-PAM 1	0.0018	0.14	0.10	85.4	9.82
II	HPG-g-PAM 2	0.0018	0.14	0.20	87.3	7.98
III	HPG-g-PAM 3	0.0018	0.14	0.30	88.9	6.02
IV	HPG-g-PAM 4	0.0018	0.14	0.40	89.5	4.86
V	HPG-g-PAM 5	0.0018	0.14	0.50	93.4	2.96
VI	HPG-g-PAM 6	0.0018	0.21	0.10	83.6	10.84

^a Calculated on the basis of monosaccharide units (MSU): 1 mole of MSU = 544 g.

^b % Conversion = [(wt of graft copolymer - wt. of polysaccharide)/wt of acrylamide monomer] × 100.

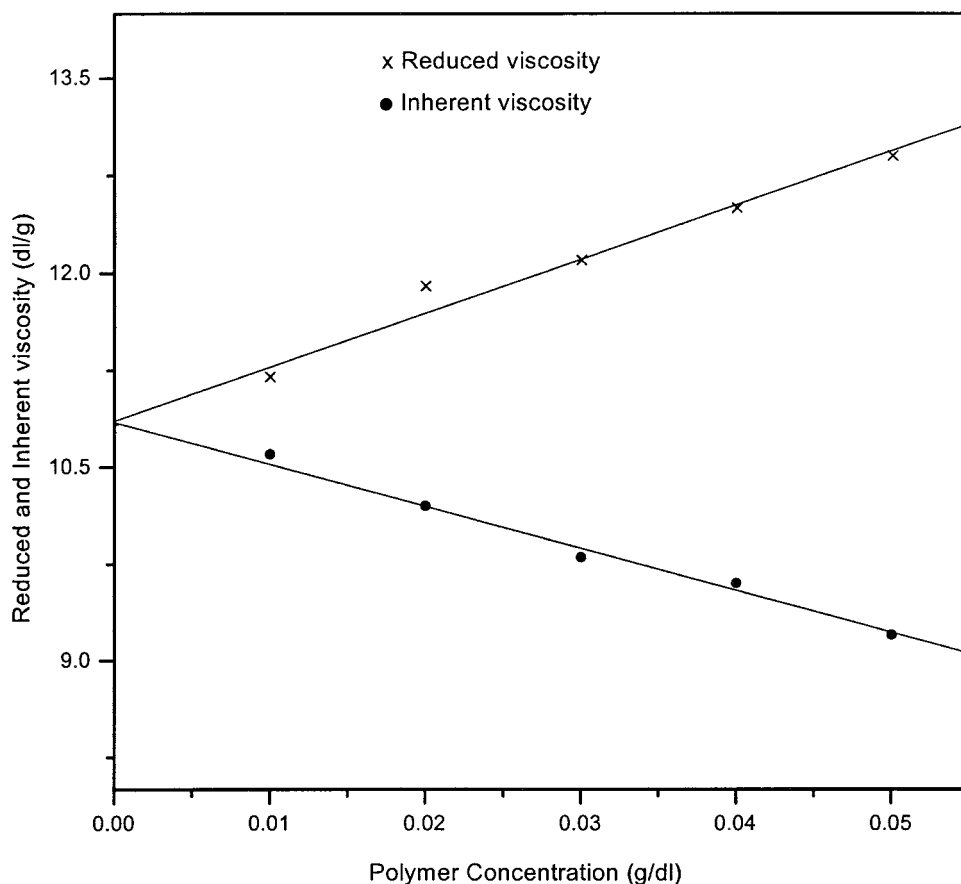


Figure 2 Intrinsic viscosity measurement of HPG-g-PAM 6.

Redcroft (STA 625) thermal analyzer in nitrogen instrument atmosphere. A heating rate of 10°C/min was employed.

Flocculation

Flocculation tests of various suspensions were carried out on a standard flocculation jar apparatus (supplied by M. B. Instruments, Mumbai, India). The turbidity measurement was carried out with the Digital Nephelo Turbidity Meter 132, procured from Systronics (Ahmedabad, India); 0.25 wt % suspensions of kaolin, iron ore, and silica (prepared by mixing 1 g in 400 cm³ of distilled water) were used for flocculation study. The suspensions were taken in each of four 1-L beakers and the flocculants were added in solution form. The following procedure was uniformly applied to all suspensions. Immediately after the addition of flocculant, the suspension was stirred at a constant speed of 75 rpm for 2 min, followed by stirring at 25 rpm for 5 min. The flocs were then allowed to settle down for 10 min. At the end

of the settling period, the turbidity of the supernatant liquid was measured. The dose of flocculants was varied from 0.025 to 1.0 ppm, calculated with respect to the total weight of the solution.

RESULTS AND DISCUSSION

Synthesis and Characterization of Graft Copolymers

Graft copolymers based on HPG have been synthesized by grafting PAM onto HPG by a radical polymerization technique in aqueous medium using a ceric ion initiation system. A number of methods are available for initiating grafting sites on a polysaccharide backbone^{20,24}; however a ceric ion-induced redox initiation method¹⁹ has been preferred. This is because the redox process initiates free radical sites^{25,26} exclusively on the polysaccharide backbone, which reduces the homopolymer formation. Similar results are also obtained by Deshmukh et al.²⁷⁻²⁹ Further, the

acrylamide and ceric ammonium ion concentrations are kept below 2.0 and 0.1M, respectively (within the limits of Owen and Shen³⁰) to ensure proper grafting and absence of homopolymerization. However, the minute quantity of homopolymer (PAM) was removed by extraction method discussed earlier. The maximum PAM formation was never found more than 1–2% and was confirmed by IR. In synthesizing the series of graft copolymers based on HPG and PAM, the aim was to develop graft copolymers with varying number and length of grafted PAM chains. With grafting PAM chains onto the polysaccharide backbone, two extreme situations are possible. One can have either a large number of short PAM chains or a small number of long PAM chains. In the former case, the original compact shape of polysaccharide would not be changed to a greater extent because of the presence of a large number of short PAM chains. This would result in lower hydrodynamic volume. By contrast, presence of small number of longer PAM chains would change the shape of polysaccharide to a greater extent, thus retaining its larger hydrodynamic volume. This would be reflected again in its high intrinsic viscosity value. The intrinsic viscosity value, which is a measure of hydrodynamic volume of the polymer in solution, is lower for a branched polymer than a linear polymer of similar molecular weight. This has been reflected in the corresponding intrinsic viscosity values of the series of graft copolymers. In the first series (sl. no. I–V), it has been observed that there is a sharp fall in the intrinsic viscosity as we go down the series (Table II). This is attributable to the formation of a large number of shorter polyacrylamide chains on increasing the ceric ammonium nitrate concentration and keeping acrylamide concentration constant. When we compare HPG-g-PAM 6 with other graft copolymers in the series, i.e., with HPG-g-PAM 1, an increase in intrinsic viscosity is expected because of the increase in acrylamide concentration at the constant CAN concentration.

The grafting is confirmed by IR spectroscopy. From the IR spectra [Fig. 3(a)], it is evident that HPG shows a broad absorption band³¹ at 3434 cm^{-1} , which is the region for the hydrogen-bonded OH groups. Two bands at ~ 1162 and 2924 cm^{-1} are assigned to C–O and C–H stretching, respectively. Two strong bands around 1080 and 1018 cm^{-1} are caused by $\text{CH}_2\text{--O--CH}_2$ stretching. In the case of graft copolymer HPG-g-PAM 6 [Fig. 3(c)], apart from these bands, additional bands at 1679, 1642, 1405, and 600–800 cm^{-1} are present.

The bands around 1679 and 1642 cm^{-1} are attributable to amide-I (CO stretching) and amide-II (NH bending) of the amide group of PAM. C–N stretching band appears at 1405 cm^{-1} . The bands within the range 600–800 cm^{-1} are for the N–H wagging vibrations. These above mentioned bands in the graft copolymer are also present in the case of PAM [Fig. 3(b)], but at slightly different absorption frequencies. However, in case of PAM a sharp band at ~ 1724 cm^{-1} is observed, which might be due to the presence of free acid groups. As acrylamide and PAM were previously removed from the products, the presence of above mentioned bands in the graft copolymer is a strong proof of grafting.

The grafting is also supported by thermal analysis studies. The thermogravimetric traces for HPG, PAM, and HPG-g-PAM 6 in nitrogen atmosphere are shown in Figure 4. In HPG, two distinct regions are observed where the weight is being lost. The initial weight loss up to 100°C is to be attributed to absorbed moisture in the sample. The decomposition of the polymer starts at 280°C and is a single-step degradation reaction. The TGA curve for PAM shows a characteristic distinct pattern from the base polysaccharide, i.e., HPG. Here, after the initial loss of weight because of a small amount of moisture, there is a continuous loss of weight with increased temperature up to 240°C. The degradation after that is due to the loss of NH_2 groups in the form of ammonia with the formation of imide groups via cyclization.³² In the case of HPG-g-PAM 6, the degradation of polymer takes place in two stages. The first stage decomposition (280–380°C) is for the degradation of both HPG and PAM chain. Starting from 380°C to 400°C decomposition of the cyclized product is observed. From the resulting curves, it is obvious that the graft copolymer (HPG-g-PAM 6) is more stable compared with the base polysaccharide (HPG) and PAM.

Flocculation Study

The flocculation performance of various grades of graft copolymers was compared in 0.25 wt % kaolin, iron ore, and silica suspensions. The results are shown in Figures 5–7, respectively. In each case, the turbidity of supernatant liquid after flocculation was plotted against polymer concentration. It is obvious from the results that the performance of HPG-g-PAM 6, which contains fewer but longer PAM chains (as evidenced from the intrinsic viscosity values), is better than that of

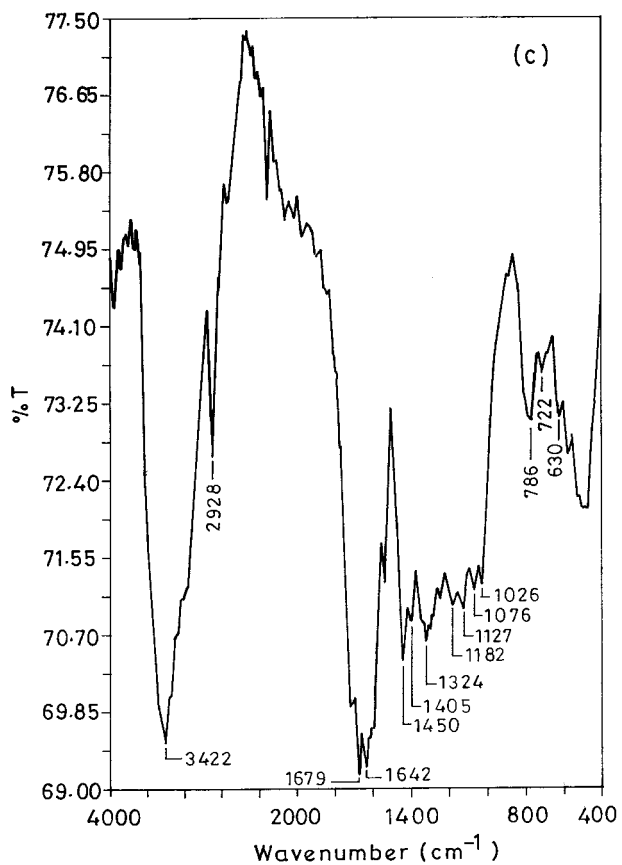
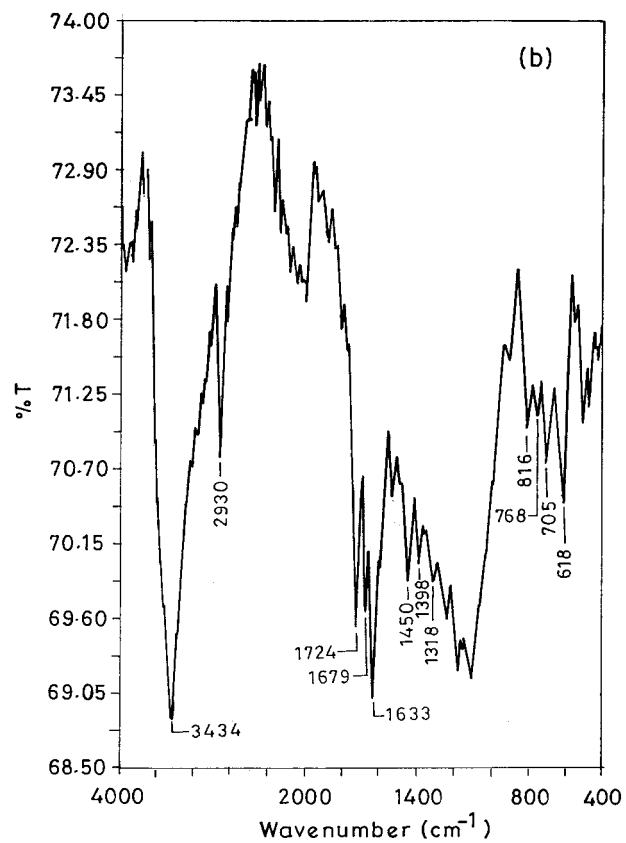
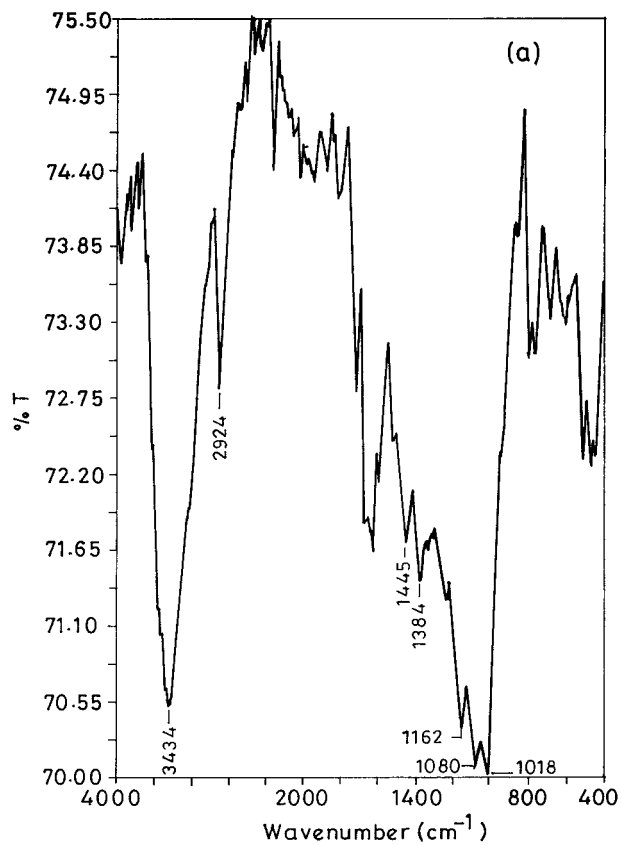


Figure 3 IR spectra of (a) hydroxypropyl guar gum (HPG), (b) polyacrylamide (PAM), and (c) HPG-g-PAM 6.

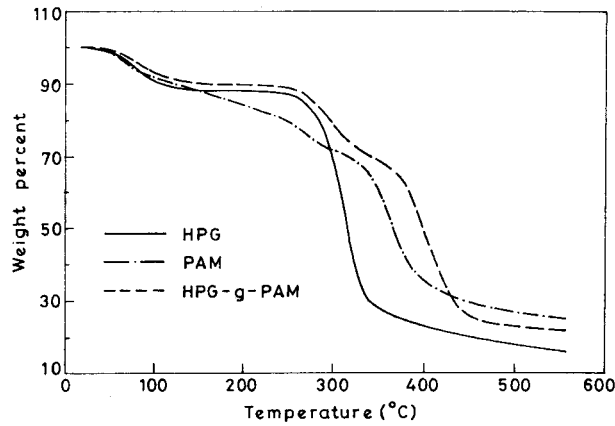


Figure 4 TGA curves of hydroxypropyl guar gum (HPG), polyacrylamide (PAM), and HPG-g-PAM 6.

other graft copolymers in all the three suspensions.

The two major mechanisms of flocculation by polymers are charge neutralization and bridging. For “non-ionic flocculants, the flocculation is caused by polymer bridging”³³ — here there can be no charge neutralization, so that bridging is the only mechanism. The controversy concerning the bridging and charge neutralization mechanisms of aggregating aqueous suspensions by the adsorption of water-soluble polymers is long

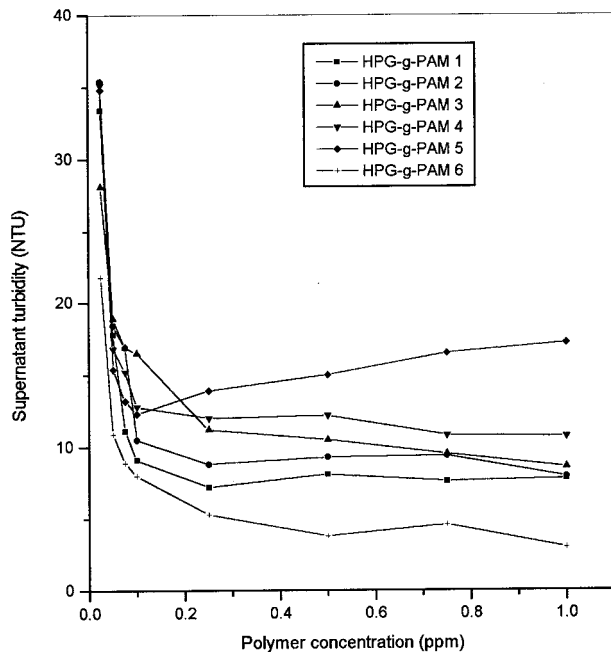


Figure 5 Comparison of flocculation efficiency of the six graft copolymers (HPG-g-PAM 1 with HPG-g-PAM 6) in 0.25 wt % kaolin suspension.

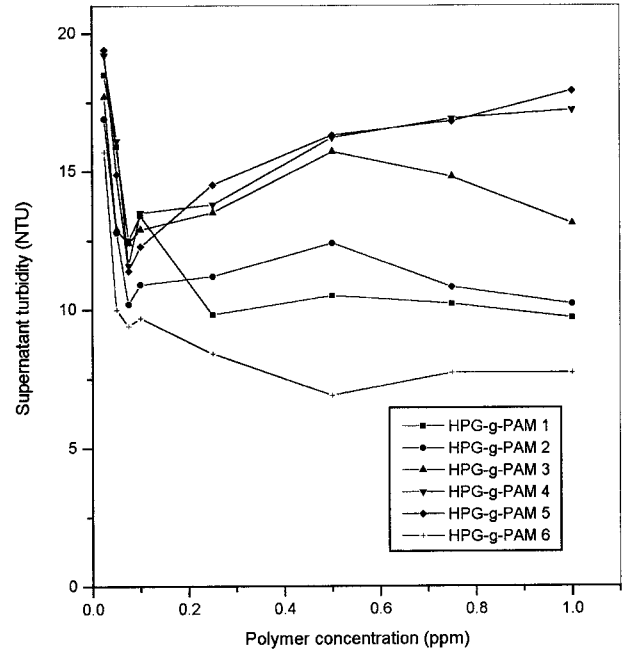


Figure 6 Comparison of flocculation efficiency of the six graft copolymers (HPG-g-PAM 1 with HPG-g-PAM 6) in 0.25 wt % iron ore suspension.

standing. In the early experimental and theoretical investigations, La Mer and his group³⁴ were prominent in advocating bridging. The bridging

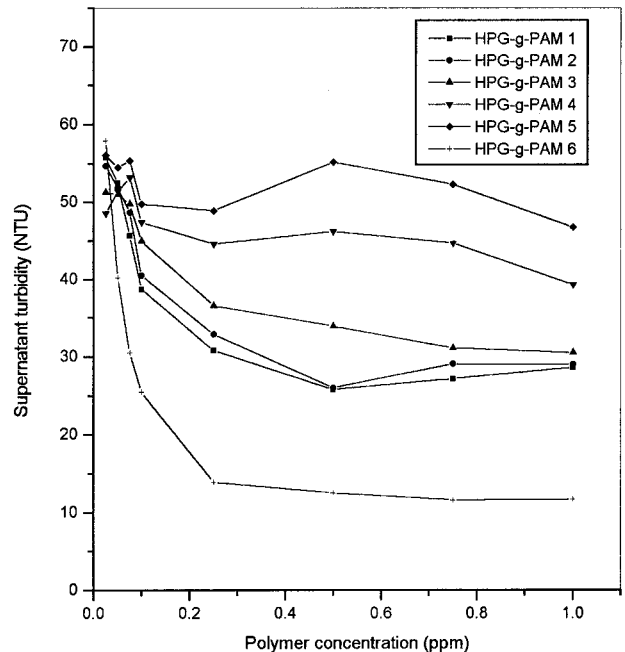


Figure 7 Comparison of flocculation efficiency of the six graft copolymers (HPG-g-PAM 1 with HPG-g-PAM 6) in 0.25 wt % silica suspension.

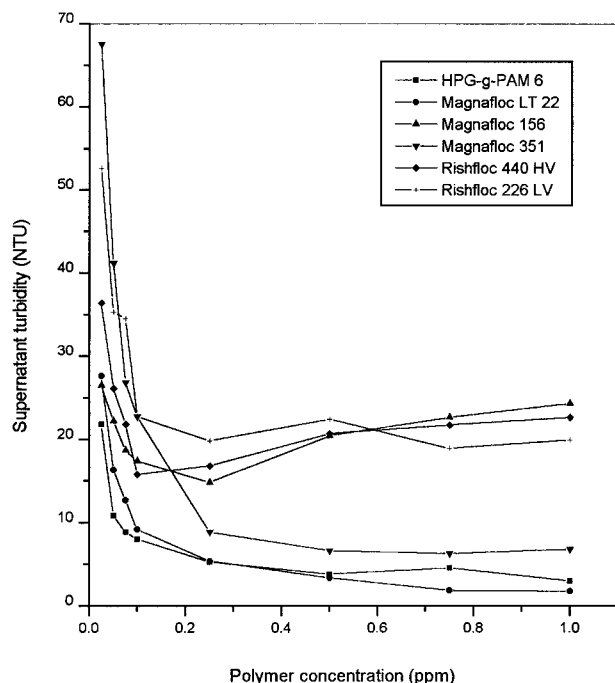


Figure 8 Comparison of flocculation efficiency of HPG-g-PAM 6 with Magnafloc LT 22, Magnafloc 156, Magnafloc 351, Rishfloc 440 HV, and Rishfloc 226 LV in 0.25 wt % kaolin suspension.

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. Hence, the polymers with longer chains would be more effective than that with shorter chains. Since of all the graft copolymers HPG-g-PAM 6 has longer PAM chains, it shows better flocculation performance compared to others having relatively shorter PAM chains. The experimental results are in line with the observations made by Michaels³⁵ and Rath and Singh.⁹

The flocculation performance of HPG-g-PAM 6 was compared with five commercial flocculants, namely, Magnafloc LT 22, Magnafloc 156, Magnafloc 351, Rishfloc 440 HV, and Rishfloc 226 LV in various suspensions. The results are shown in Figures 8–10. HPG-g-PAM 6 was deliberately

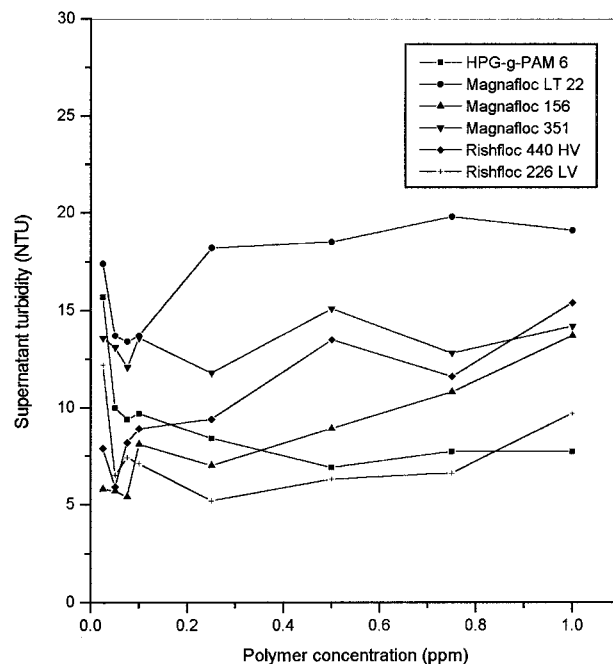


Figure 9 Comparison of flocculation efficiency of HPG-g-PAM 6 with Magnafloc LT 22, Magnafloc 156, Magnafloc 351, Rishfloc 440 HV, and Rishfloc 226 LV in 0.25 wt % iron ore suspension.

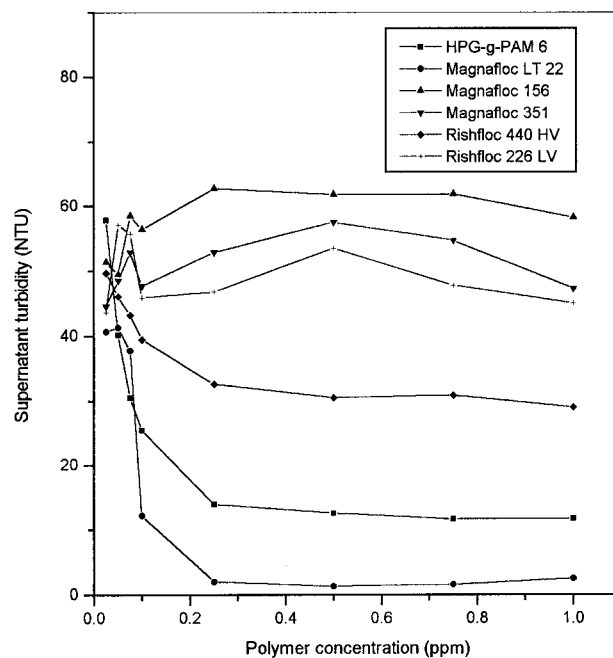


Figure 10 Comparison of flocculation efficiency of HPG-g-PAM 6 with Magnafloc LT 22, Magnafloc 156, Magnafloc 351, Rishfloc 440 HV, and Rishfloc 226 LV in 0.25 wt % silica suspension.

chosen because of its fewer and longer PAM chains among all the graft copolymers. With the kaolin suspension (Fig. 8), HPG-g-PAM 6 shows a better performance than others except Magnafloc LT 22. Its performance is at par with the Magnafloc LT 22. With the iron ore suspension (Fig. 9), only Rishfloc 226 LV shows a markedly better performance than the graft copolymer. It may be noted that Magnafloc 156 and Rishfloc 440 HV, work appreciably at lower doses, show an upward trend at higher doses. With the silica suspension (Fig. 10), only Magnafloc LT 22 shows the better performance than the graft copolymer. However, the graft copolymer still shows better performance than some other commercial flocculants. The reason for better flocculating power of the graft copolymers over the linear polymers is for the effective bridging as already discussed. In the case of linear polymers, the polymer segments attach to the surface in trains, project into the solution as tails, or to form a part of loops, which link trail together. In this way they can form bridges between the colloidal particles to form flocs.³⁶ In the case of graft copolymers due to the better approachability of the grafted PAM chains, they can easily bind the colloidal particles through bridging and form the flocs. This type of intense bridging is not possible in the case of linear polymers.

CONCLUSIONS

From the above experimental studies, it can be concluded that by grafting PAM chains onto HPG, a modified naturally occurring polysaccharide, an effective flocculating agent can be developed for the treatment of wastewater. Except for a few commercial flocculants, the graft copolymers show the better flocculation characteristics. Among the grafted products, those having fewer and longer PAM chains are better than those with shorter PAM chains.

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