

Synthesis, Characterization, and Flocculation Characteristics of Hydrolyzed and Unhydrolyzed Polyacrylamide Grafted Xanthan Gum

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ABSTRACT: The partial hydrolysis of xanthan gum-g-polyacrylamide was carried out in alkaline medium. Four grades of partially hydrolyzed products were synthesized by varying the reaction parameters. The neutralization equivalents of these products were determined by titration with standard sodium hydroxide solution. The flocculation characteristics of all the hydrolyzed graft copolymers and the unhydrolyzed xanthan gum-g-polyacrylamide were determined in 5 wt % iron ore and kaolin suspensions. The

partially hydrolyzed product with neutralization equivalent of 1000 g showed better performance than that of other partially hydrolyzed products, but all hydrolyzed products exhibited poorer performance than that of the unhydrolyzed product in flocculation. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1411–1419, 2004

Key words: polysaccharides; graft copolymers; water-soluble polymers; hydrolysis; neutralization equivalent

INTRODUCTION

Recently, water-soluble polymers of high molecular weight have drawn much attention because of their various practical applications. High molecular weight synthetic polymers, such as polyacrylamides, are very effective flocculating agents. However, these polymers are unstable in shear fields and thus lose their flocculating effectiveness. Natural polymers, such as polysaccharides, exhibit good resistance to shear degradation. However, they are less-effective flocculating agents compared with synthetic polymers and their aqueous solutions are susceptible toward biodegradation. Intensive investigations have been carried out in the authors' laboratory for almost two decades.^{1–4} Singh et al. synthesized graft copolymers of acrylamide with amylose, amylopectin, carboxymethyl cellulose, guar gum, hydroxy propyl guar gum, sodium alginate, starch, and xanthan gum.^{5–9} It has been observed by Singh and coworkers that the graft copolymers of polysaccharides and polyacrylamide show better flocculating efficiency than that of the conventional polysaccharide and synthetic polymer-based flocculants.^{10–12} It was also pointed out by Singh that the enhanced flocculation characteristics are attributed to the ease in approachability of flexible polyacrylamide chains grafted onto rigid robust polysaccharide

backbones to the contaminant particles in the effluents.

It has been observed in some cases that partially hydrolyzed polyacrylamide shows better flocculating behavior than that of polyacrylamide itself.¹³ Partially hydrolyzed starch-g-polyacrylamide and partially hydrolyzed sodium alginate-g-polyacrylamide showed similar behavior.^{14,15} These polymers are generally prepared by treatment with alkali. Polyacrylamides acquire a polyelectrolyte character on hydrolysis, and as a result the viscosity of the solution increases because of coil expansion.

The xanthan polymer backbone is identical to that of cellulose, but the unique character of xanthan gum (XG) is derived from the trisaccharide side chain on alternate sugar units. This chain is composed of a glucuronic acid salt between mannose acetate and a terminal mannose unit. A pyruvate is attached to about 60% of these terminal units. The glucuronic acid and pyruvic acid groups on the side chains give xanthan gum its anionic charge. The interaction of these side chains with the polymer backbone and with each other determines the properties of xanthan gum solutions. Xanthan gum is an anionic polyelectrolyte with a β -(1 \rightarrow 4)-D-glucopyranose glucan backbone with side chains of (3 \rightarrow 1)- α -linked D-mannopyranose-(2 \rightarrow 1)- β -D-glucuronic acid-(4 \rightarrow 1)- β -D-mannopyranose on alternating residues. It has many special characteristics and applications. It is used as a rheology control agent in aqueous systems and as a stabilizer for emulsions and suspensions. Its various areas of applications extend from oil drilling to the food industry. The structure of xanthan gum is given in Figure 1.

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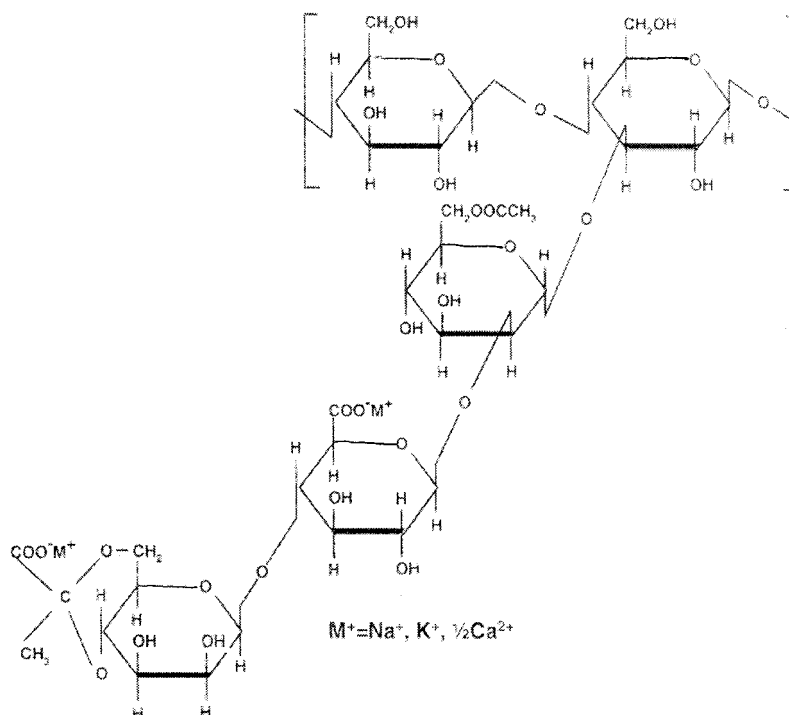


Figure 1 Structure of xanthan gum.

In previous reports, the synthesis and drag-reduction characteristics of xanthan gum-g-polyacrylamide (XG-g-PAM) were reported.¹⁶⁻¹⁸ The present article reports the synthetic details of partially hydrolyzed XG-g-PAM formulations (XG-2 to XG-5) and flocculation performance in 5 wt % iron ore and kaolin suspensions. The objective of partial hydrolysis of the grafted XG-g-PAM (XG-1) was to establish the relation between the flocculation efficiency with expansion of the grafted flexible PAM chains. As a result of hydrolysis, the $-CONH_2$ groups of PAM chains are converted to $-COOH$ groups. Thus, negatively charged groups already present and newly formed negatively charged groups repel each other, resulting in chain expansion.¹⁹

EXPERIMENTAL

Materials

Xanthan gum was procured from Carl Roth GmbH (Karlsruhe, Germany). Acrylamide was procured

from E. Merck (Darmstadt, Germany). Ceric ammonium nitrate (CAN) was obtained from Loba Chemie (Bombay, India). Acetone and sodium hydroxide were procured from E. Merck (Bombay, India). Nitric acid, analar grade, was procured from BDH India (Mumbai, India). The iron ore sample was collected from Kiriburu mines (India). Kaolin was supplied by C. D. Pharmaceutical Works (Howrah, India). The commercial flocculants Rishfloc 440HV and Rishfloc 226LV were procured from Rishav Chemicals Pvt. Ltd. (India). Xanthan gum was used after extraction with 95% ethyl alcohol for 80 h. All other chemicals were used without further purification.

Synthesis of xanthan gum-g-PAM

Xanthan gum-g-PAM was synthesized according to previous reports¹⁶⁻¹⁸ by a solution polymerization technique using CAN as catalyst.

TABLE I
Synthetic Details of Alkaline Hydrolysis of XG-g-PAM

Polymer	Volume of 1N NaOH (cm ³)	Reaction temperature (°C)	Reaction time (h)	N.E. ^a (g)
XG-1	0	0	0	2000
XG-2	10	50	1	1000
XG-3	50	50	1	666.67
XG-4	50	50	3	571.43
XG-5	50	70	3	333.34

^a N.E., neutralization equivalent.

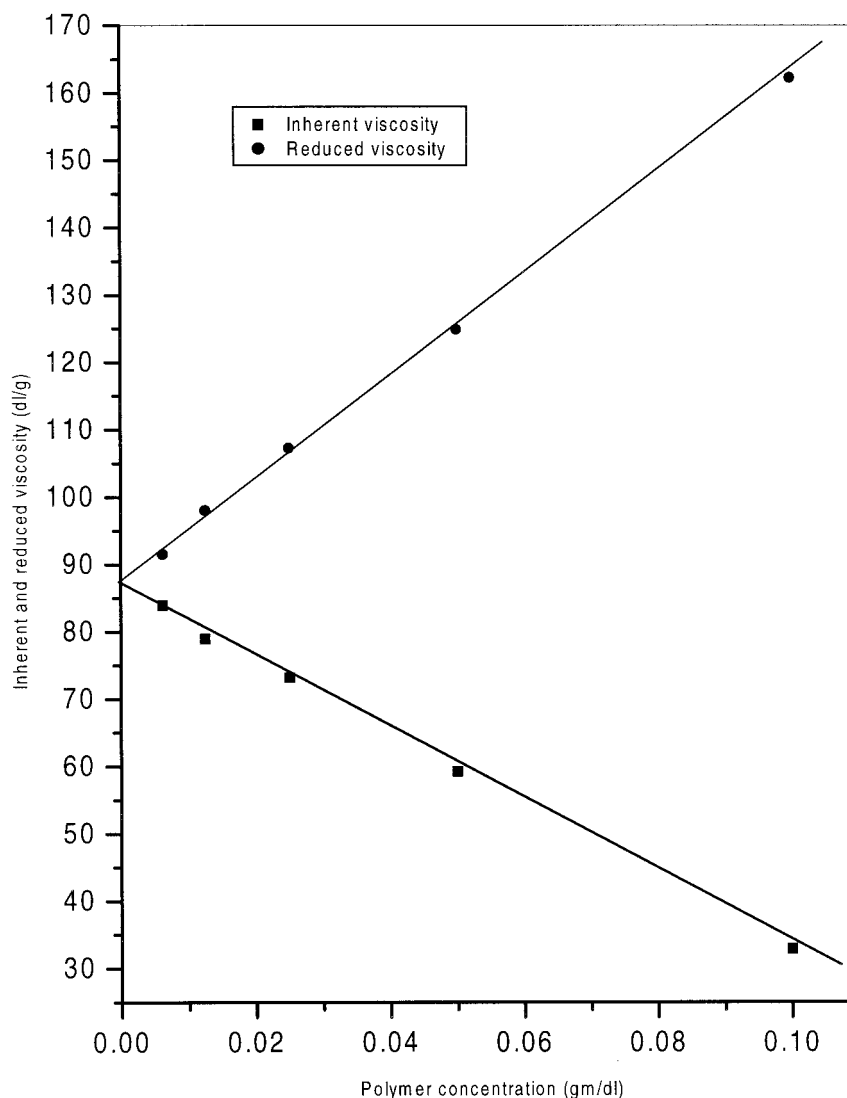


Figure 2 Intrinsic viscosity measurement curve for hydrolyzed XG-g-PAM.

Alkaline hydrolysis of xanthan gum-g-PAM

XG-g-PAM (2 g) was dissolved in 200 mL distilled water and then a required amount of NaOH was added to it. The mixture was placed in a thermostated water bath at a specified temperature. At the end of the required reaction time the content of the reaction was poured into 400 mL ethyl alcohol. The product was filtered and washed with an ethanol water mixture (70 : 30 by volume) and finally with ethanol, after which it was dried. Four grades of hydrolyzed products were obtained by varying the reaction conditions. The results are shown in Table I. The hydrolyzed polymers were designated XG-2, XG-3, XG-4, and XG-5.

Determination of neutralization equivalent (N.E.) of the hydrolyzed polymer

The N.E. value is the equivalent weight of the acid, as determined by titration with standard base.^{15,20}

A 0.2-g sample of each of the XG-1 to XG-5 polymers was dissolved in 150 mL of distilled water in a conical flask. After that 40 mL 0.1N HCl was added to each of the five solutions. The flasks were kept for 4 h under this condition. Then the solutions were back titrated with standard 1N NaOH to neutralize the excess HCl. During alkaline hydrolysis, $-\text{COONa}$ groups were generated. To generate the $-\text{COOH}$ groups, HCl was added to the mixture. Because HCl is much stronger than the organic acid, it will be neutralized. Organic acids are not dissociated in the pres-

TABLE II
Intrinsic Viscosity Values

Polymer	Intrinsic viscosity
Xanthan gum	32.5
XG-g-PAM (XG-1)	11.01
Hydrolyzed XG-g-PAM (XG-2)	87.5

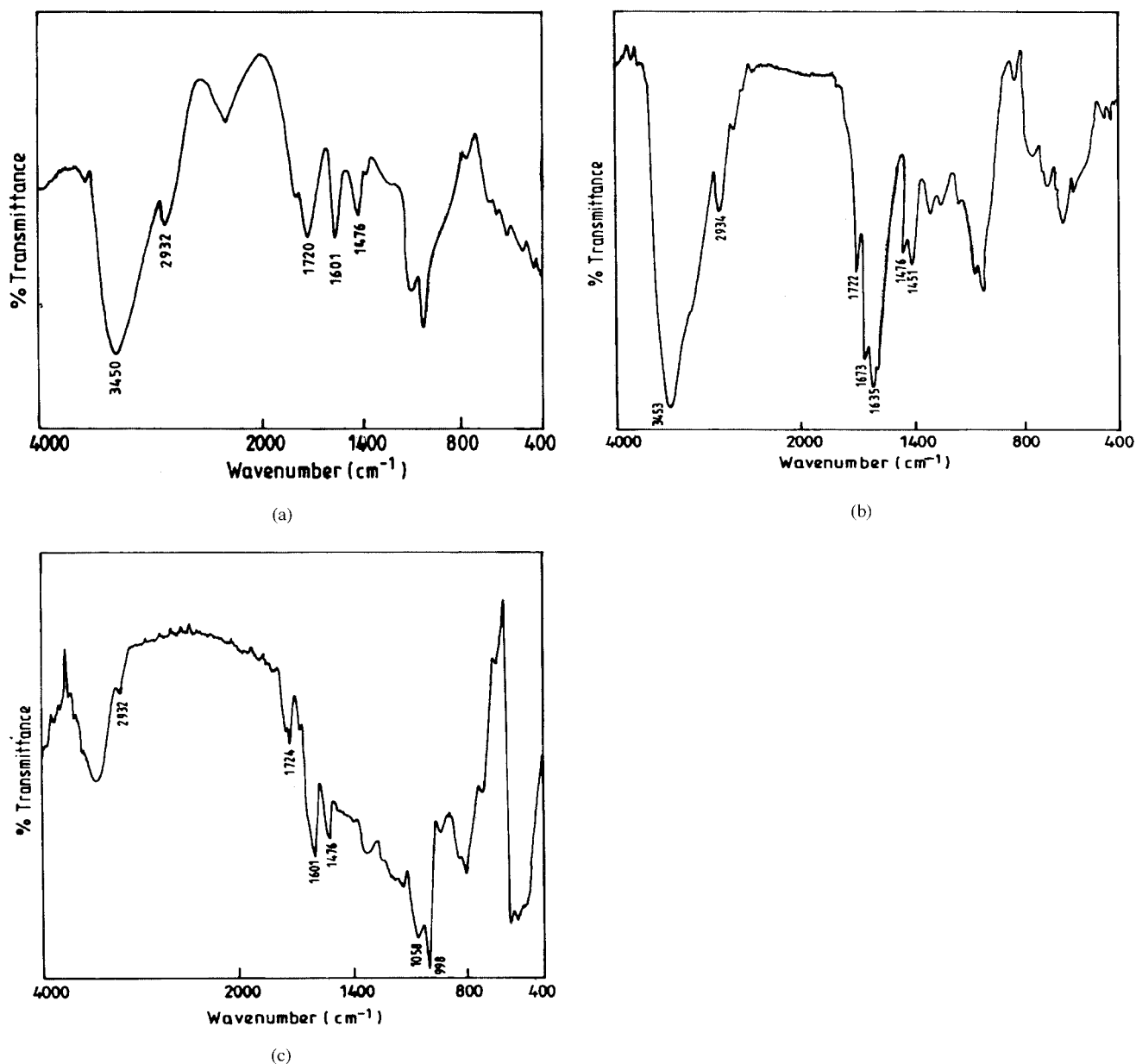


Figure 3 (a) IR spectra of xanthan gum; (b) IR spectra of XG-g-PAM; (c) IR spectra of hydrolyzed XG-g-PAM.

ence of HCl because of the common ion effect. HCl (40 mL of 0.1N) was also titrated by 1N NaOH solution. The difference between the titer values of only HCl in polymer solutions gives the volume of alkali required for titrating the acid formed during acidification of the polymer. The N.E. values of polymers XG-1 to XG-5 are given in Table I.

Viscosity measurements

Viscosity measurements of the aqueous solutions of XG-g-PAM (XG-1) and hydrolyzed XG-g-PAM (XG-2) were carried out with the use of a Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA) at 30°C.

The time of flow was measured for various solutions at 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. Specific viscosity was calculated from the relation $\eta_{sp} = \eta_{rel} - 1$. Then, the reduced viscosity (η_{sp}/C), and the inherent viscosity $[\ln(\eta_{rel}/C)]$ were calculated, where C is the polymer concentration in g/dL. The intrinsic viscosity was obtained (from the point of intersection) after extrapolation of two plots [i.e., η_{sp}/C versus C , and $\ln(\eta_{rel}/C)$ versus C] to zero concentration, as shown in Figure 2. The intrinsic viscosity values of graft copolymer and hydrolyzed graft copolymer are reported in Table II.

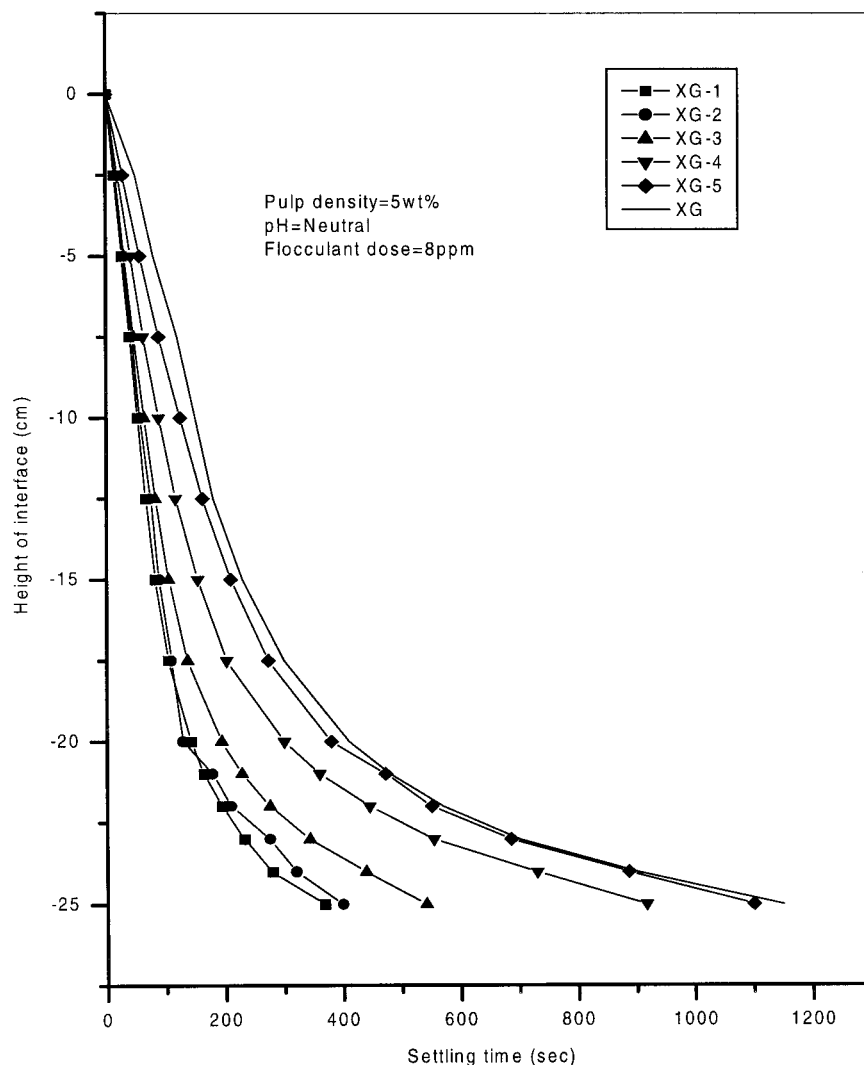


Figure 4 Comparison of flocculation efficiency of xanthan gum, XG-g-PAM, and hydrolyzed XG-g-PAM in 5 wt % kaolin suspension.

Infrared spectroscopy

A Perkin-Elmer 630 IR spectrophotometer (Perkin Elmer Cetus Instruments, Norwalk, CT) was used to record the IR spectra within the range of $4000\text{--}400\text{ cm}^{-1}$. The IR spectra of XG-g-PAM were recorded in the solid state using the KBr pellet method.

Flocculation studies

Flocculation study of the polymers was carried out in 5 wt % iron ore and kaolin suspensions by a column test in a 100-mL stoppered graduated cylinder. The concentration of the polymer stock solution was 10^{-4} g/mL . The flocculation characteristics of all the grades were compared and the grade showing the best settling efficiency was determined. The flocculation characteristic of the best hydrolyzed grade was compared with those of several commercial flocculants such as Rishfloc 440HV and Rishfloc 226LV, which are anionic

and nonionic in nature, respectively. The standard jar test technique was also followed for the flocculation study. The turbidity versus polymer dosage graph was then plotted.

RESULTS AND DISCUSSION

IR spectroscopy

The grafting and hydrolysis of the grafted product were confirmed by IR spectroscopy. From the IR spectra [Fig. 3(a), (b), and (c)], it is evident that xanthan gum shows a broad absorption peak at 3450 cm^{-1} , which is the region for the hydrogen-bonded OH groups. Two peaks, one around 1601 and the other at 1476 cm^{-1} , are attributed to the COO^- groups. In the case of graft copolymer XG-g-PAM, apart from these bands, additional bands at 1679 , 1635 , 1451 , and $600\text{--}800\text{ cm}^{-1}$ are present. The bands around 1679 and 1635 cm^{-1} are attributed to amide-I (CO stretching) and

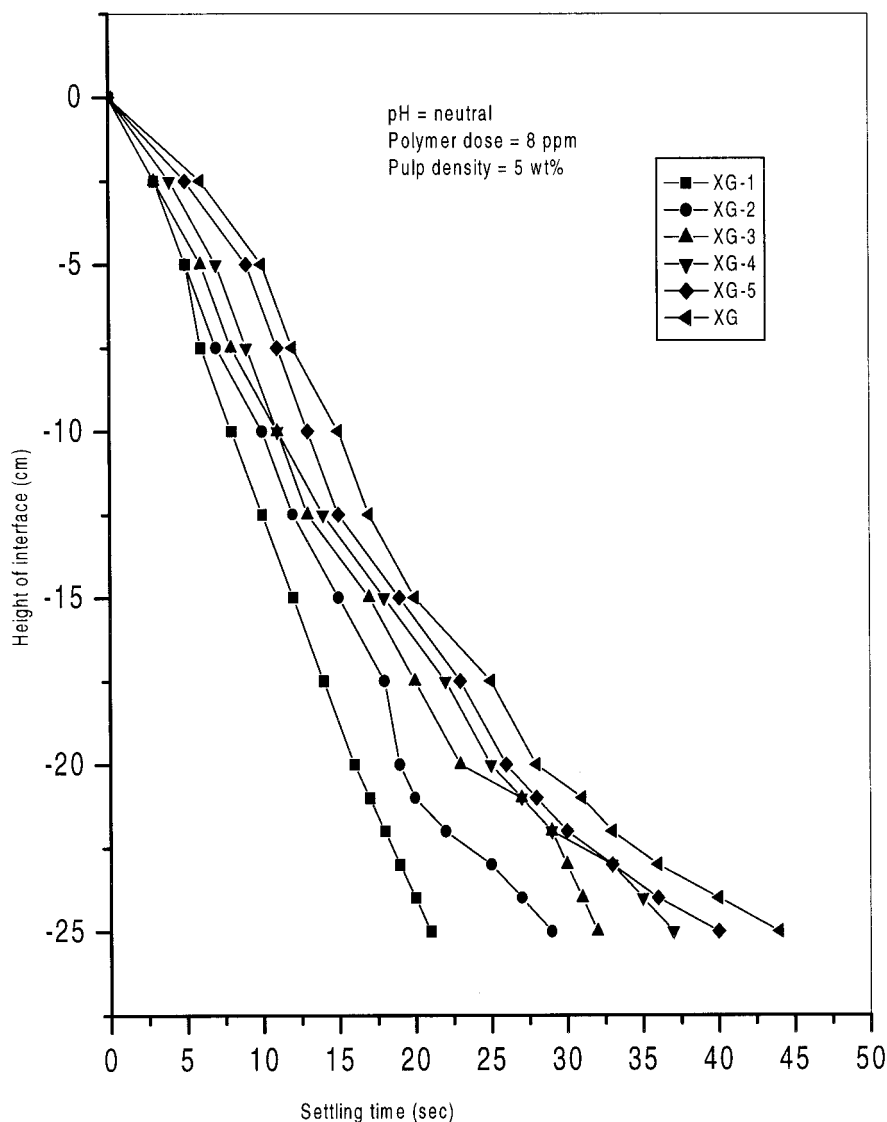


Figure 5 Comparison of flocculation efficiency of xanthan gum, XG-g-PAM, and hydrolyzed XG-g-PAM in 5 wt % iron ore suspension.

amide-II (N—H bending) of the amide group of PAM. The peak at 3453 cm^{-1} in XG-g-PAM is attributed to the overlap of N—H stretching band of amide group and O—H stretching band. The C—N stretching band appears at 1451 cm^{-1} . The bands within the range $600\text{--}800\text{ cm}^{-1}$ are attributed to the N—H wagging vibrations.

In the case of hydrolyzed XG-g-PAM, the sharp peak at 3453 cm^{-1} is absent, thus proving the absence of the N—H band. The peaks at 1601 and 1476 cm^{-1} correspond to asymmetric and symmetric stretching of COO^- group, respectively. These factors prove the hydrolysis of the grafted product.

Intrinsic viscosity calculations

The intrinsic viscosity values of xanthan gum, grafted xanthan gum, and hydrolyzed grafted xanthan gum

are shown in Table II. The intrinsic viscosity value, which is a measure of the hydrodynamic volume of the polymer in solution, is lower for a branched polymer than that for a linear polymer of similar molecular weight. From intrinsic viscosity calculations, it was found that hydrolyzed XG-g-PAM has a higher intrinsic viscosity than that of XG-g-PAM, which may be explained by extension of the backbone chain, which occurs as the result of electrostatic repulsion of carboxylic groups.

Study of neutralization equivalent

In hydrolyzing the graft copolymers of xanthan gum and polyacrylamide, the aim is to straighten and expand the flexible polyacrylamide chains. During the treatment with sodium hydroxide solution, the following reactions were expected to occur: (1) saponifi-

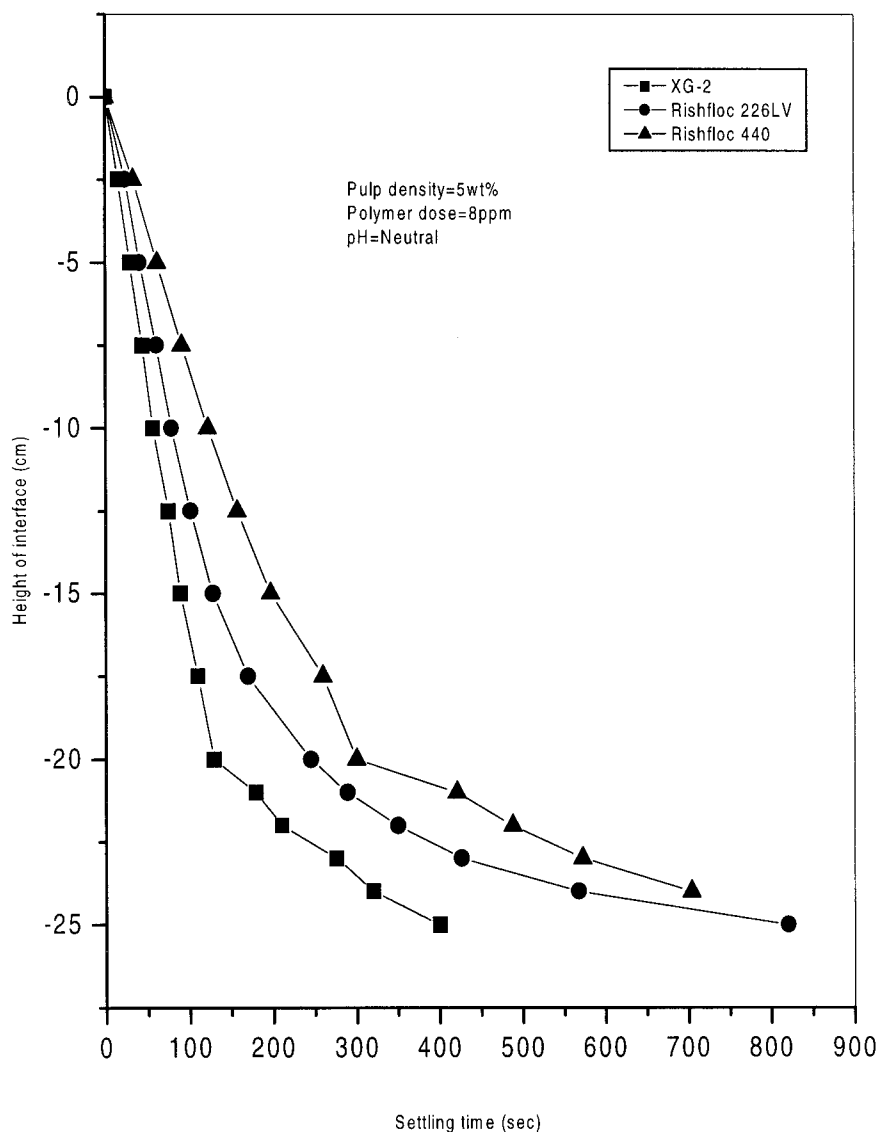


Figure 6 Comparison of flocculation efficiency of XG-g-PAM and some commercial flocculants in 5 wt % kaolin suspension.

cation of amide groups to carboxyl groups and (2) deetherification of the polysaccharide and depolymerization reactions of the polyacrylate component of the graft copolymer. The extent of these reactions depends on the treatment conditions. During alkaline hydrolysis of poly(acrylamide) starch graft copolymer, it was shown by Khalil et al.¹⁴ that the use of sodium hydroxide concentrations up to 1N and temperatures between 80 and 90°C, the saponification reaction (conversion of $-\text{CONH}_2$ group into $-\text{COOH}$) was the only reaction.¹⁴ Upon use of higher concentrations of alkali, the deetherification and depolymerization reactions can occur simultaneously with the saponification reaction. From Table I it is obvious that in the present case, the concentrations of alkali are well below 1N and thus, under the mentioned reaction conditions, saponification is likely to be the only reaction. From N.E. measurements of the partially hydrolyzed XG-g-PAM and unhydrolyzed XG-g-PAM, it can be con-

cluded that the carboxylic acid content of the hydrolyzed samples depends on the NaOH concentration as well as the duration and temperature of the treatment. The carboxylic acid content increased on increasing reaction duration and/or reaction temperature or NaOH concentration. N.E. gradually decreases from XG-2 to XG-5. N.E. values are a function of the number of alkaline groups on hydrolyzed XG-g-PAM and represent the molecular weight of the acid/base. During alkaline hydrolysis of the amide groups, the molecular weight of the polymer would remain the same (because one $-\text{OH}$ group is incorporated after the expulsion of $-\text{NH}_3$). Thus a greater number of carboxylic acid anion groups will lower the neutralization equivalent value.

Xanthan gum is an anionic polyelectrolyte derivative of cellulose. After hydrolysis anionic groups are generated. This leads to repulsion with the existing anionic groups and chain expansion occurs. The expansion of

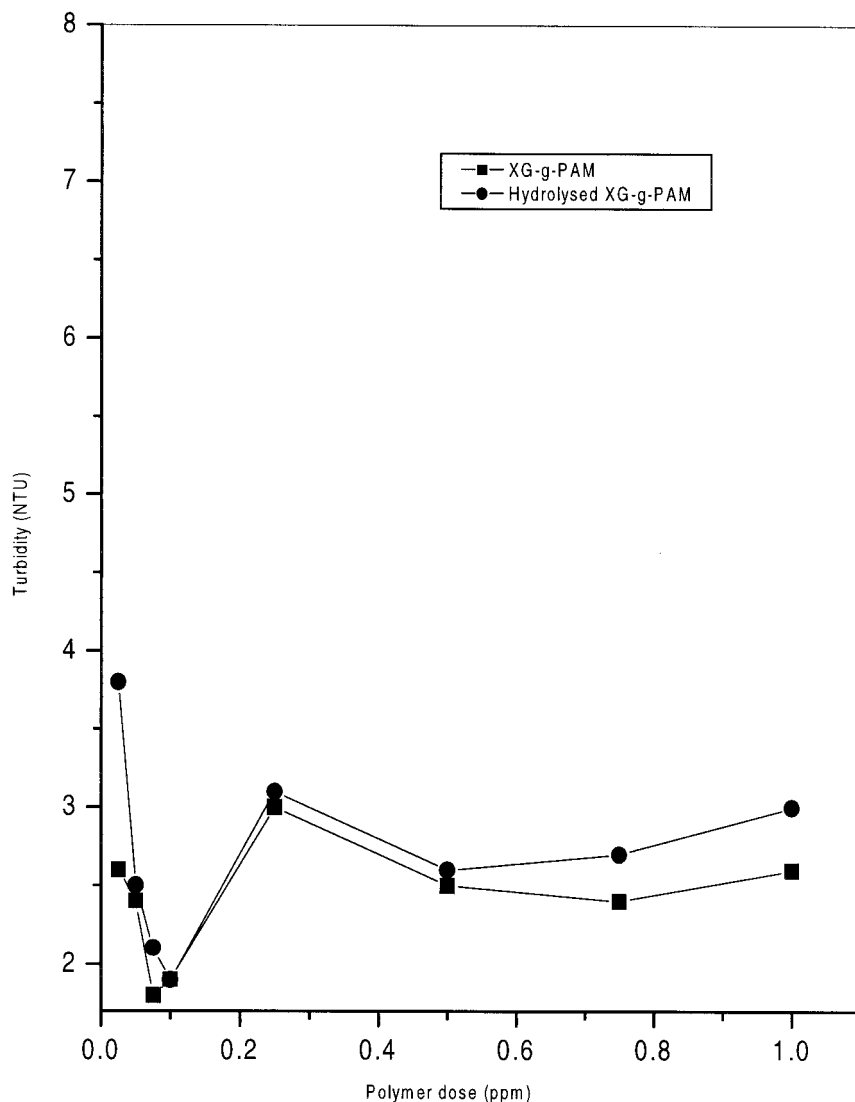


Figure 7 Comparison of flocculation characteristics of XG-g-PAM and hydrolyzed XG-g-PAM in 1 wt % iron ore suspension.

chains increases the approachability of polyacrylamide branches to the contaminants and thus increases the flocculation. However, increasing the negative charge by hydrolysis also increases repulsion of the polymer chains with negatively charged particles of kaolin and iron ore. Thus, the effect of chain extension is annulled by the addition of anionic moieties, resulting in the decrement of the flocculation characteristics.

Flocculation studies

The flocculation performance of XG and XG-1 to XG-5 in 5 wt % kaolin suspension is depicted in Figure 4. Figure 5 shows a comparison of the flocculation efficiency in 5 wt % iron ore suspension. In these figures, the height of the interface between the solid and liquid is plotted against time. The starting point of interface is depicted as zero, and thus the descending interface is depicted in negative scale. The flocculating perfor-

mance of a particular polymer can be correlated with settling velocity. The larger the settling velocity of the floc-containing contaminants, the greater will be its flocculation performance. From Figures 5 and 6, it is evident that with increasing carboxylic content of the hydrolyzed graft copolymer, the flocculation performance decreases. During conversion of XG-1 (N.E. = 2000 g) to XG-2 (N.E. = 1000 g), PAM chains expand because of repulsion with the existing negative charges on the polysaccharide backbone, which may increase flocculation. However, with an increasing number of anionic moieties, the repulsion between polymers and contaminants also increases, resulting in a decrease of flocculation performance. Overall, the latter effect overshadows the effect of chain expansion, and thus there is a decrement in flocculation performance on hydrolysis of grafted xanthan gum.

In Figure 6 the flocculation performance of XG-2 is compared with that of commercially available floccu-

lants, Rishfloc440 and Rishfloc 226LV. It is found that XG-2 shows better performance than that of these two commercial flocculants.

In Figure 7 the flocculation performance is expressed in terms of turbidity using the jar-test method. Initially there is decrement in turbidity attributed to flocculation at a low dose of flocculant. As the dose increases the deflocculation occurs and thus there is decrease in the turbidity of supernatant liquid versus concentration of the flocculent (which is very normal in the concentration versus turbidity plots). This deflocculation is attributed to repulsion of the added flocculant with the flocculant already adsorbed on the particle surfaces.²¹ The experimental error is ± 0.1 NTU (nephelometric turbidity unit, a measure of the clarity of water), which cannot be shown clearly in the Figure 7. The lower the turbidity, the better the flocculating agent. The efficiency of XG-g-PAM and hydrolyzed XG-g-PAM was tested in 1 wt % iron ore suspension. It was found that XG-g-PAM shows lower turbidity than that of hydrolyzed XG-g-PAM for the reasons indicated earlier.

CONCLUSIONS

From the above study, it can be concluded that it is possible to control the carboxyl content by controlling the reaction parameters (e.g., reaction temperature, time, and concentration of alkali). The neutralization equivalent values can also be evaluated.

The hydrolyzed product with a neutralization equivalent of 1000 g shows better flocculation efficiency than that of other hydrolyzed grades but poorer than that of grafted xanthan gum. Thus it can be inferred that partial alkaline hydrolysis of xanthan gum-g-polyacrylamide does not increase the flocculation efficiency because of the repulsion between existing negative charges and newly formed charges, which overshadows the increment in flocculation with the chain expansion.

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