

Synthesis, Characterization, Flocculation, and Rheological Characteristics of Hydrolyzed and Unhydrolyzed Polyacrylamide-Grafted Poly(vinyl alcohol)

S. Krishnamoorthi, R. P. Singh

Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India

Received 26 September 2003; accepted 18 November 2004

DOI 10.1002/app.21755

Published online 11 May 2006 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Graft copolymers of poly(vinyl alcohol) and polyacrylamide (PVA-g-PAM) were synthesized using a ceric ion-induced solution polymerization technique at 28°C. Three grades of graft copolymers were synthesized with varying acrylamide concentrations. Three grades of hydrolyzed products of PVA-g-PAM were synthesized with varying concentrations of sodium hydroxide solution. Hydrolyzed and unhydrolyzed PVA-g-PAM were characterized by viscometry, X-ray diffractometry, infrared spectroscopy, and thermal analysis. Rheological investigation was also carried out on the aqueous solutions of various samples. The flocculation characteristics of various materials were

investigated by the use of jar and settling tests in 0.25 and 5 wt %, respectively, using kaolin and iron ore suspensions. Among the series of graft copolymers, the one with fewest but longest PAM chains showed superior performance. The flocculation characteristics of the best-performing graft copolymer were compared with those of various commercially available flocculants in the two suspensions under investigation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2109–2122, 2006

Key words: biodegradable; graft copolymers; radical polymerization; rheology; water-soluble polymers

INTRODUCTION

The development of industry and agriculture essential for worldwide communities is associated with occupational hazards and environmental pollution. Moreover, the global scenario of energy crisis, environmental concern, and depleting raw material resources have forced scientists and technologists to develop materials from renewable agriculture or plant resources, which can protect the environment.

Flocculation is a process of bringing together small particles to form larger aggregates, often highly porous in nature. The commercial flocculants are of two kinds: organic¹ and inorganic.² Of the two, organic flocculants are more effective because they are required only in minute quantities, they produce less sludge, and they do not require any pH adjustments. Organic flocculants may be natural or synthetic. Starch, alginic acid, and guar gum are among the natural polymers used in flocculation. Among the synthetic flocculants commonly used are polymers such as polyacrylamide and poly(ethylene oxide)³ in the nonionic category, poly(diallyldimethylammonium chloride)⁴ in the cationic category, and poly(styrenic

sulfonic acid) in the anionic category. Natural polymers have the advantages of low cost and biodegradability. The biodegradability of natural polymers as such also acts as a drawback in that it reduces the storage life and the flocculation performance. On the other hand, synthetic polymers are highly efficient and can be tailored to the needs of a particular application. However, their biggest disadvantage is their shear degradability.

In the authors' laboratory⁵ many graft copolymers have been synthesized by grafting polyacrylamide onto carboxymethyl cellulose (CMC),⁶ guar gum,⁷ starch,⁸ and xanthan gum,⁹ for example, and both their shear stability and drag reduction efficiencies have been investigated. Later studies on the flocculation behavior of graft copolymers indicated that they are more effective than the linear polymers. It was postulated by Singh¹⁰ that graft copolymers are more effective than linear polymers because of the greater approachability of dangling polyacrylamide-grafted chains onto rigid polysaccharides to the contaminants in various suspensions.

In the present study, the flocculation characteristics of graft copolymers of poly(vinyl alcohol) and polyacrylamide (PVA-g-PAM) were investigated in various suspensions. Their performance was compared with the laboratory-synthesized graft copolymer amylopectin-grafted polyacrylamide (AP-g-PAM), and also with various commercially available flocculants.

Correspondence to: S. Krishnamoorthi (skmoorthi@bhu.ac.in)

TABLE I
Details of Sources and Chemical Nature of Commercial Flocculants and Suspensions (Kaolin and Iron Ore)

| Flocculant | Chemical nature | Source | | | |
|-------------------|-------------------------------------|---|--------------------|----------------------------------|----------------|
| Magnafloc 156 | Anionic | Ciba Geigy Special Chemical Division (Bradford, UK) | | | |
| Magnafloc 351 | Nonionic | | | | |
| Sample | Source | % Fe ₂ O ₃ | % SiO ₂ | % Al ₂ O ₃ | % Other oxides |
| Kiriburu Iron ore | Kiriburu Mine (Orissa, India) | 61.40 | 3.84 | 6.63 | 28.13 |
| Kaolin | C. D. Pharmaceutical (Howra, India) | 0.25 | 46.25 | 39.13 | 14.37 |

The reasons for choosing PVA are that it is easily available, water-soluble, and a biodegradable polymer. PVA itself has flocculation properties. It is a highly polar polymer compared to other polymers that have been studied in the laboratory. It is also available in grafted form like other polymers and PVA is a good protective colloid for aqueous emulsions.

It has been observed in some cases that partially hydrolyzed PAM shows better flocculating behavior than that of PAM itself.¹¹ Partially hydrolyzed AP-g-PAM,¹² CMC-g-PAM,¹³ sodium alginate-g-PAM,¹⁴ and starch-g-PAM,¹⁵ have also shown similar behavior. These polymers are generally prepared by treatment with alkali. With hydrolysis, the polyacrylamides acquire a polyelectrolyte character. As a result the viscosity of solution increases as a result of coil expansion. The present article also reports the synthetic details of partially hydrolyzed PVA-g-PAM and its flocculation performance in kaolin and iron ore suspensions. The objective of partial hydrolysis of the grafted PVA-g-PAM was to be establish the relation between the flocculation efficiency with expansion and straightening of the grafted flexible PAM chains. As a result of hydrolysis, -CONH₂ groups of PAM chains are converted to the -COOH groups. Thus adjacent negatively charged groups repel each other, so the chains will be expanded and straightened. The performance of hydrolyzed PVA-g-PAM is compared with that of unhydrolyzed PVA-g-PAM.

EXPERIMENTAL

Materials

Poly(vinyl alcohol) was purchased from Thomas Baker (Chemicals) (Mumbai, India). Acrylamide was purchased from E. Merck-Schuchardt (Darmstadt, Germany). Ceric ammonium nitrate, sodium hydroxide, and acetone were obtained from E. Merck (Mumbai, India). Nitric acid was supplied by E. Merck-Worli (Mumbai, India). Hydroquinone was obtained from S. D. Fine Chemicals (Mumbai, India). Only two commercial flocculants, Magnafloc 156 and Magnafloc 351, were used for comparison. Magnofloc 156 and Magnafloc 351 are characteristically anionic and nonionic, respectively. Kaolin was supplied by C. D. Pharmaceutical Works (Howrah, India). Iron ore was obtained from Kiriburu Mines (Orissa, India). The details of sources and chemical nature of the commercial flocculants and suspensions are given in Table I. All the chemicals received were used as received without further purification.

Synthesis

The graft copolymers were synthesized by a ceric ion-induced redox initiation method.¹⁶ The synthetic details are given in Table II. The following procedure was used for the synthesis of graft copolymers of poly(vinyl alcohol) and acrylamide. Poly(vinyl alco-

TABLE II
Synthetic Details of Graft Copolymers

| Polymer | PVA (g) | Acrylamide (mol) | CAN (mM) | % Conversion ^a | Intrinsic viscosity (dL/g) | M _w (×10 ⁶) |
|-----------|---------|------------------|----------|---------------------------|----------------------------|------------------------------------|
| Grade I | 1 | 0.109 | 0.25 | 77.62 | 4.8 | 1.31 |
| Grade II | 1 | 0.137 | 0.25 | 92.10 | 25.38 | 10.5 |
| Grade III | 1 | 0.21 | 0.25 | 74.32 | 6.25 | 1.8 |
| PVA | — | — | — | — | 0.763 | 0.11 |

^a % Conversion = [(wt of graft copolymer - wt of PVA)/wt of acrylamide] × 100.

TABLE III
Synthetic Details of Alkaline Hydrolysis of PVA-g-PAM

| Polymer | Volume of I (N) NaOH (cc) | Reaction Temperature (°C) | Reaction time (h) |
|---------|---------------------------|---------------------------|-------------------|
| Hyd-I | 10 | 50 | 1 |
| Hyd-II | 15 | 50 | 1 |
| Hyd-III | 25 | 50 | 1 |

hol) (1 g) and various quantities of acrylamide were dissolved in 300 mL of distilled water in an Erlenmeyer flask. The solution was stirred by a magnetic stirrer and the flask was sealed with a septum stopper. The solution was then flushed with nitrogen gas, introduced through a hypodermic needle, and another needle was introduced inside the stopper for the outlet of gas. The solution was then continuously stirred with a magnetic stirrer and the nitrogen gas was bubbled for 30-min intervals. The required quantity of ceric ammonium nitrate, dissolved in 1M nitric acid, was injected into the solution through a hypodermic needle and then nitrogen gas flushing was continued

for a further 30 min. Bubbling of nitrogen gas was stopped after the flask was sealed with Teflon tape and the needles were removed from the stopper. The temperature of the reaction was maintained at $30 \pm 0.10^\circ\text{C}$ by immersing the flask in a constant-temperature water bath. The reaction was terminated by injecting 0.5 mL of aqueous saturated hydroquinone solution. The polymer solution was precipitated in an excess of acetone and then the product was dried in a vacuum at 35°C .

Synthesis of polyacrylamide was achieved using the same experimental conditions as used for synthetic graft copolymer.

Purification of graft copolymers by solvent extraction

The extraction of occluded PAM was carried out by solvent extraction using a mixture of formamide and acetic acid (1:1 by volume). The detailed procedure was as follows: 3 g each of graft copolymer was charged to a 250-mL beaker. Then 100 cm^3 of the

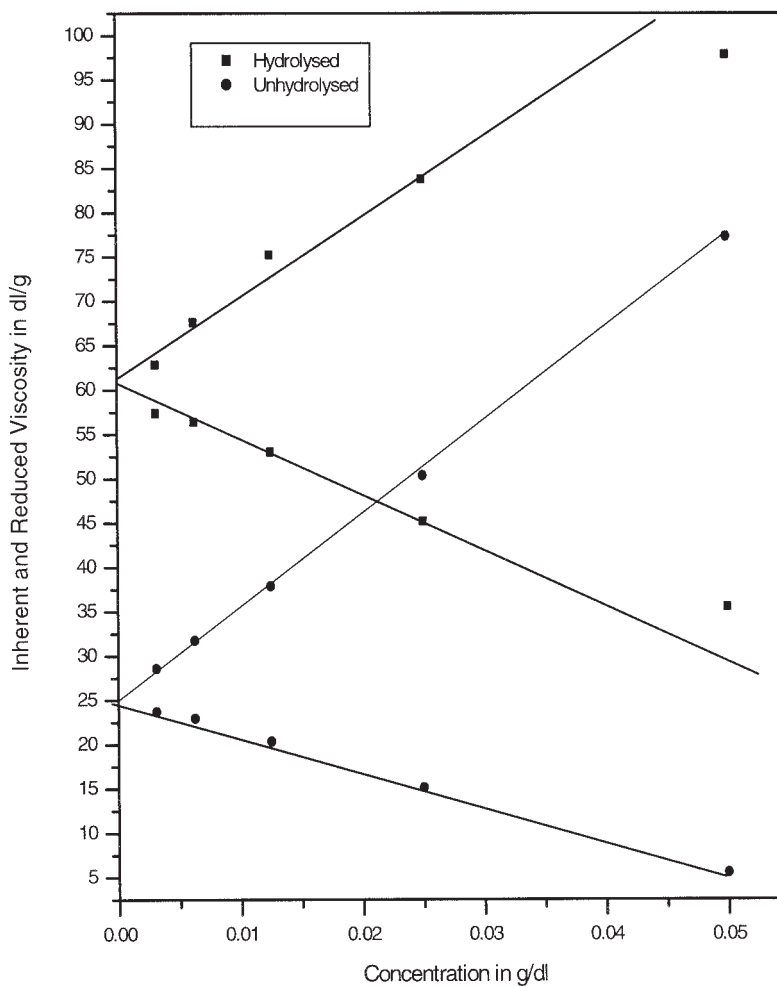


Figure 1 Intrinsic viscosity measurement of hydrolyzed and unhydrolyzed PVA-g-PAM.

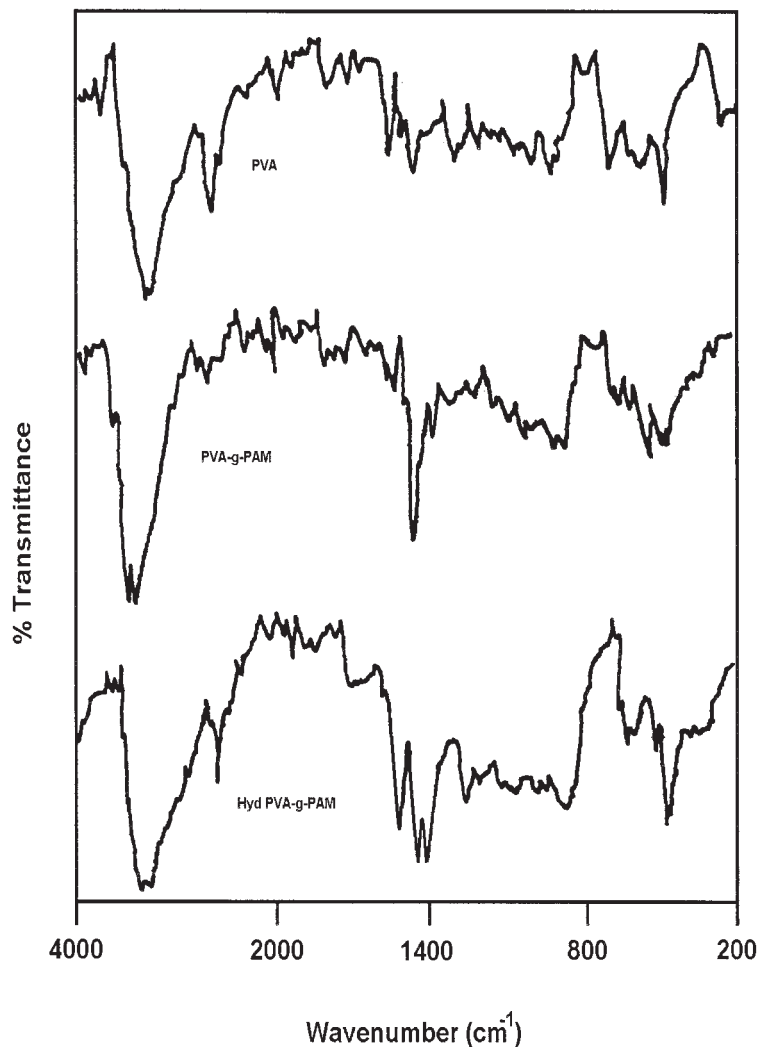


Figure 2 IR spectra of poly(vinyl alcohol), PVA-g-PAM, and hydrolyzed PVA-g-PAM.

solvent was added and then the mixture was maintained at 40°C for 12 h. After that the mixture was filtered using a Buchner funnel. The residue was washed 10 times with the same solvent mixture and, every time, the filtrate was checked with acetone as to verify precipitation of PAM. After washing the polymer, it was again washed with methanol to remove the solvent and kept in methanol for 24 h. It was then dried in a vacuum oven at 35°C.

Alkaline hydrolysis

Alkaline hydrolysis of PVA-g-PAM was performed as follows: 2 g of PVA-g-PAM was dissolved in 200 cm³ of distilled water, after which the requisite amount of 1N NaOH solution was added. The mixture solution was then placed in a thermostated water bath at a specified temperature. At the end of the proposed reaction time, the content of the flask was removed and poured into 1 L of ethyl alcohol. The product was

filtered and washed with an ethanol–water mixture (70 : 30 by volume), and finally with ethanol, and was then dried. Three hydrolyzed products were synthesized by varying the experimental conditions. The results are shown in Table III.

Characterization

Viscosity measurements

The intrinsic viscosity of all graft copolymers was determined from the intersection of two extrapolated (to zero concentration) plots (i.e., inherent and reduced viscosity versus concentration, respectively). A Ubbelohde viscometer (P/2739) was used. A 0.5 g sample of the polymer was dissolved in distilled water, with slow stirring, at a temperature of 60°C. The resulting solution was cooled to room temperature and the volume was made up to 100 cm³.

From the time of flow of pure solvent (t_0 , for distilled water) and the polymer solutions (t), relative

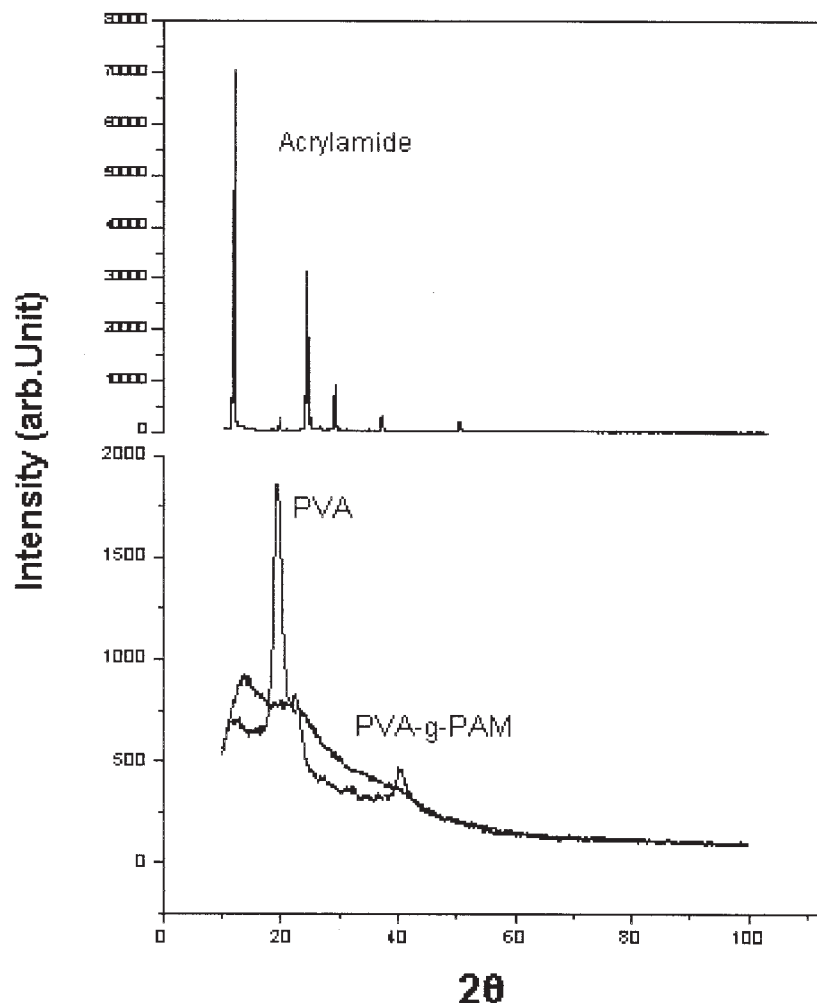


Figure 3 XRD diffractogram of acrylamide, poly(vinyl alcohol), and PVA-g-PAM.

viscosity ($\eta_l = t/t_0$) was obtained. The terms related to viscosity measurements¹⁷ are given as follows: specific viscosity = $\eta_r - l = \eta_{sp}$; reduced viscosity = $\eta_{sp}/C = \eta_{red}$; inherent viscosity = $\ln \eta_r/C = \eta_{inh}$; and intrinsic viscosity = $(\ln \eta_{sp}/C)_{C \rightarrow 0} = [\eta]$. The intrinsic viscosity values of graft copolymer and hydrolyzed products are given in Table II. The intrinsic viscosity measurement curves are shown in Figure 1.

Infrared spectroscopy

One of the above grades of graft copolymer (grade II) was subjected to IR spectral analysis. A PE-883 infrared spectrophotometer (Perkin-Elmer LAS, Buckinghamshire, UK) was used and the potassium bromide (KBr) pellet method was followed for IR study. The IR spectra of polyacrylamide (PAM), poly(vinyl alcohol), PVA-g-PAM (grade II), and hydrolyzed PVA-g-PAM are shown in Figure 2.

X-ray diffractometry (XRD)

Acrylamide, poly(vinyl alcohol), and PVA-g-PAM (grade II) were subjected to XRD analysis. The pow-

dered polymer sample was packed into a hole of 2 mm diameter in a small container made of Perspex [poly(methyl methacrylate)], about 1.5 mm thick. This piece was mounted on the specimen holder with pressure-sensitive tape so that the X-ray beam would pass through the hole. A PW 1840 diffractometer and PW 1729 X-ray generator (Philips, Eindhoven, Holland) were used for the study producing Cu-K α radiation. The results are shown in Figure 3.

Thermal analysis

The DSC analysis of all samples was carried out with a Pyris Diamond DSC apparatus (Perkin-Elmer Cetus Instruments, Norwalk, CT). DSC analysis of the samples was performed up to a temperature of 400°C, starting from room temperature, in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10°C/min. The DSC curves of PVA and both hydrolyzed and unhydrolyzed PVA-g-PAM are shown in Figure 4.

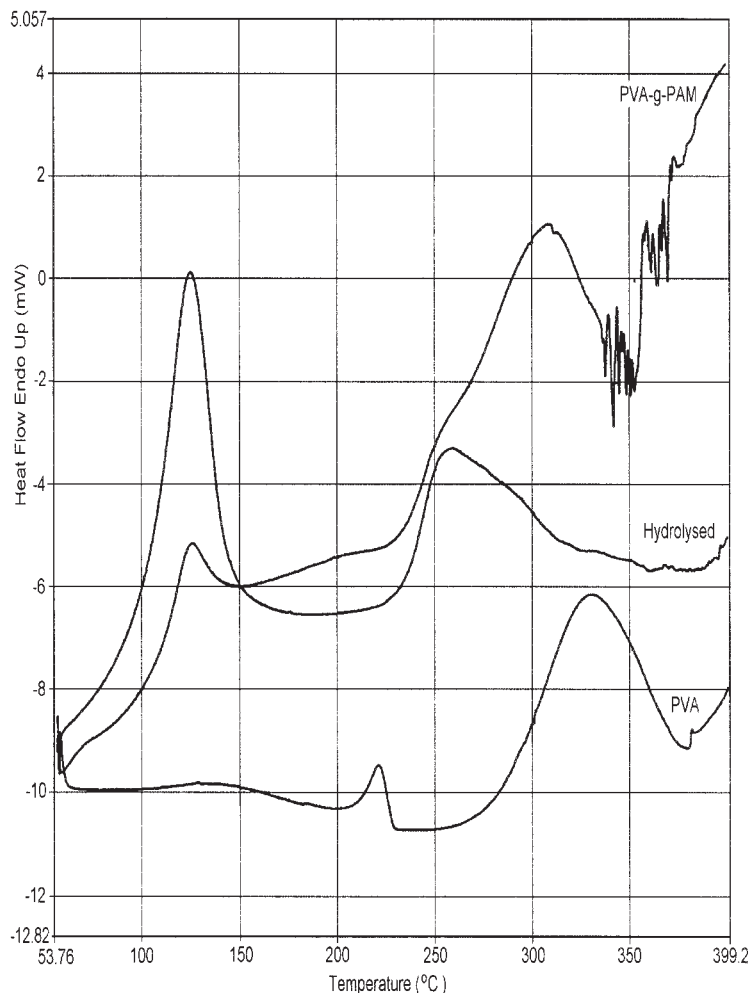


Figure 4 DSC curves of PVA and hydrolyzed and unhydrolyzed PVA-g-PAM.

Calculation of approximate molecular weight

The molecular weight of grafted chains was calculated from intrinsic viscosity, $[\eta]$, using the Mark-Houwink equation, $[\eta] = KM^\alpha$, where the K and α values depend on the nature of the polymer and solvent used. For instance, for polyacrylamide:

$$[\eta] = 6.13 \times 10^{-5}(M_w)^{0.80} \quad (1)$$

where M_w is the weight-average molecular weight.

TABLE IV
Determination of Neutralization Equivalent (NE)

| Sample | Volume of 1 (N) NaOH (V_2) (cc) | $V_1 - V_2$ (cc) | N.E |
|---------|-------------------------------------|------------------|------|
| Hyd-I | 2.25 | 0.05 | 4000 |
| Hyd-II | 2.1 | 0.2 | 1000 |
| Hyd-III | 2.2 | 0.1 | 2000 |

V_1 is the volume of 1 (N) NaOH to neutralize 40cc of HCL = 2.3 cc.

The approximate molecular weights of the graft copolymers based on this relationship are given in Table II.

Determination of neutralization equivalent

The neutralization equivalent (NE) is the equivalent of the acid as determined by the titration with standard base.¹⁸ The neutralization equivalent of an acid can be determined in the following way: Let x gm of sample of an unknown acid require y mL of z N NaOH for complete neutralization. Because each 1000 mL of the base contains z equivalents and the number of equivalents of base required equals the number of equivalent of acid present, the equivalent weight of the acid will be equal to

$$\frac{x \times 1000}{y \times z} \quad (2)$$

A sample (0.2 g) of each of the hydrolyzed products was dissolved in 150 mL of distilled water in a conical

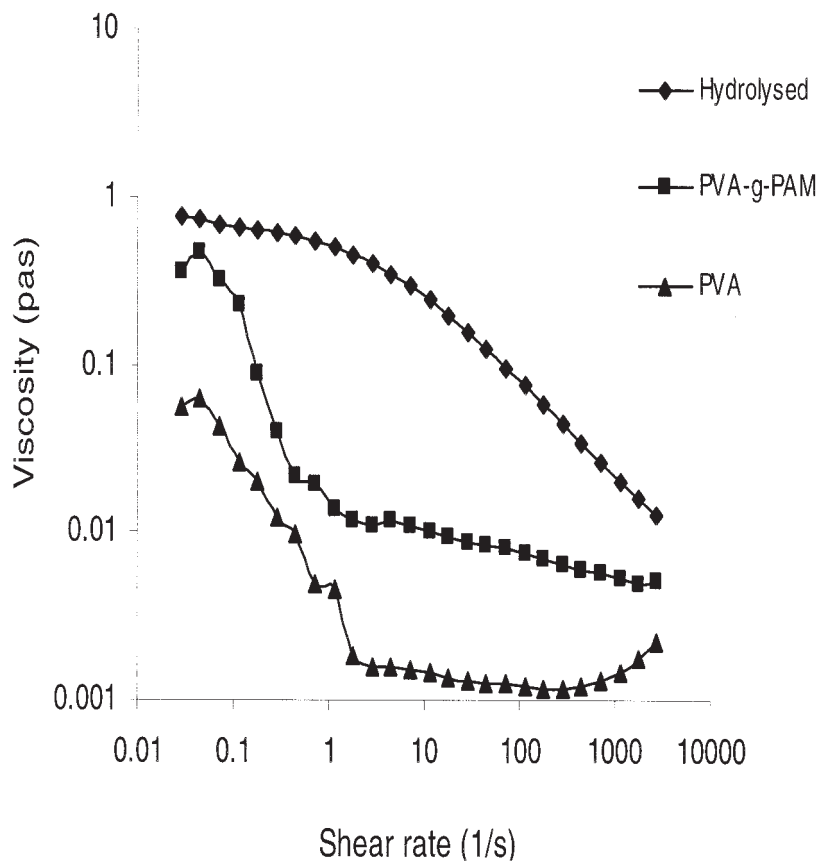


Figure 5 Viscosity versus shear rate variation plot for 0.2 wt % PVA, PVA-g-PAM, and hydrolyzed PVA-g-PAM.

flask. After that 40 cm³ of 0.1N HCl was added to each of the five solutions and maintained for 5 h under this condition. Then the solutions were back-titrated with standard 1N NaOH solutions; 40 cm³ of 0.1N HCl was also titrated by 1N NaOH solutions. The difference between the titer value of only HCl and the polymer solutions gives the volume of alkali required to titrate the acid in the polymer. The NE values of the hydrolyzed products are given in Table IV.

Rheological investigation

Using the AR-1000 rheometer (TA Instruments, New Castle, DE), the viscosity versus shear rate studies were conducted for 0.5 wt % polymer solutions of poly(vinyl alcohol), graft copolymer, and the hydrolyzed forms of PVA-g-PAM. The plot (Fig. 5) obtained from the rheometer experiment conducted clearly shows the variation of viscosity with varying shear rates.

Flocculation

Jar test. The principal purpose of a flocculation test¹⁹ procedure is to establish the optimal conditions for floc formation, although the nature of test may be

substantially influenced by process considerations. The flocculator, supplied by M. B. Flocculators (Bombay, India), consisted of six pedals on a bench connected to each other by a gear mechanism. All the pedals were simultaneously rotated by the same motor, with a provision for speed control. The following procedure was adopted uniformly in all cases: 400 mL of the flocculating suspension was charged to 1-L flocculation jars. For the synthetic suspensions, 0.25 wt % solids content was chosen. The jars were placed on the flocculator bench, and the stirrer blades were dipped in the suspension. A dilute polymer solution of 10⁻⁴ g/mL concentration was added to each jar under slow stirring condition. Immediately after addition of polymer to all the jars, the suspensions were stirred at a constant high speed of 75 rpm for 2 min followed by slow stirring at 25 rpm for 5 min. The flocs that developed during slow stirring were allowed to settle for 10 min. Clean supernatant liquid was drawn and its turbidity was measured by a digital Nephelo turbidity meter (Acma's Technologies Inc., Delhi, India). The turbidity was expressed in Nephelo turbidity units (NTU). Turbidity versus polymer dosage graph was then plotted.

Settling test. The test used a 25-mL stoppered graduated cylinder and stopwatch. The slurry sample was

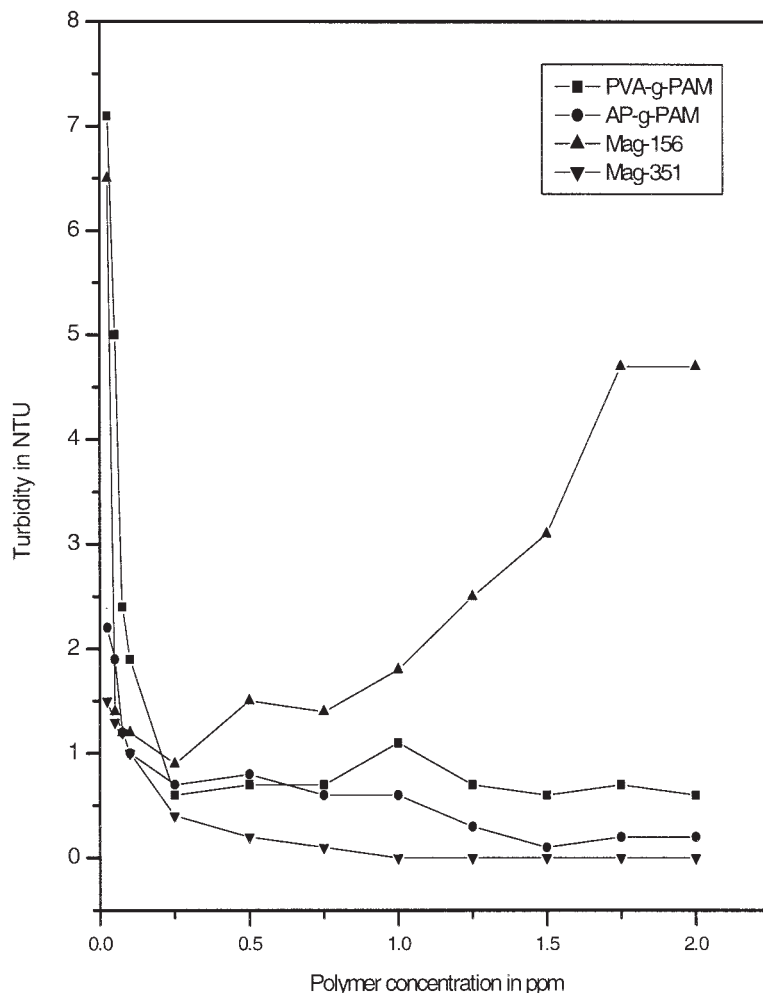


Figure 6 Flocculation performances of PVA-g-PAM and commercial flocculants in 0.25 wt % kaolin suspension.

placed in the cylinder, the chemical was added, and the cylinder was inverted 10 times. After mixing, the cylinder was set upright and the height of interface between the supernatant liquid and setting solid bed was measured over a certain time period.

RESULTS AND DISCUSSION

Synthesis and intrinsic viscosity

Table II shows the synthetic details of graft copolymers based on poly(vinyl alcohol). A series of three graft copolymers was synthesized based on poly(vinyl alcohol). The synthesis was carried out for three graded graft copolymers by varying only the acrylamide concentration, keeping the PVA and catalyst concentration fixed. The mechanism of ceric ion action involves the formation of chelate complex that decomposes to generate free-radical sites on the PVA backbone. These active free-radical sites, in the presence of acrylic monomers, generate graft copolymers. At lower concentrations of acrylamide for the given con-

stant catalyst concentration, there is a large number of grafting sites, making the average polyacrylamide chains short. On increasing the acrylamide concentration at constant CAN concentration, longer polyacrylamide chains are generated. At greater concentrations of acrylamide, the polymer chains tend once again to be smaller because of poor grafting efficiency. Thus by varying the acrylamide concentration, we obtain an optimum concentration for which an optimum grafting can be obtained with efficient polymerization of acrylamide.

It is known that the intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn is a function of the polymer molecular weight, its structure, nature of solvent, and the temperature of the medium. Keeping the other factors constant for two polymers of approximately similar molecular weight, a branched polymer will have lower hydrodynamic volume and thus a lower intrinsic viscosity compared to that of its linear counterpart. Further, along a series of branched polymers, the

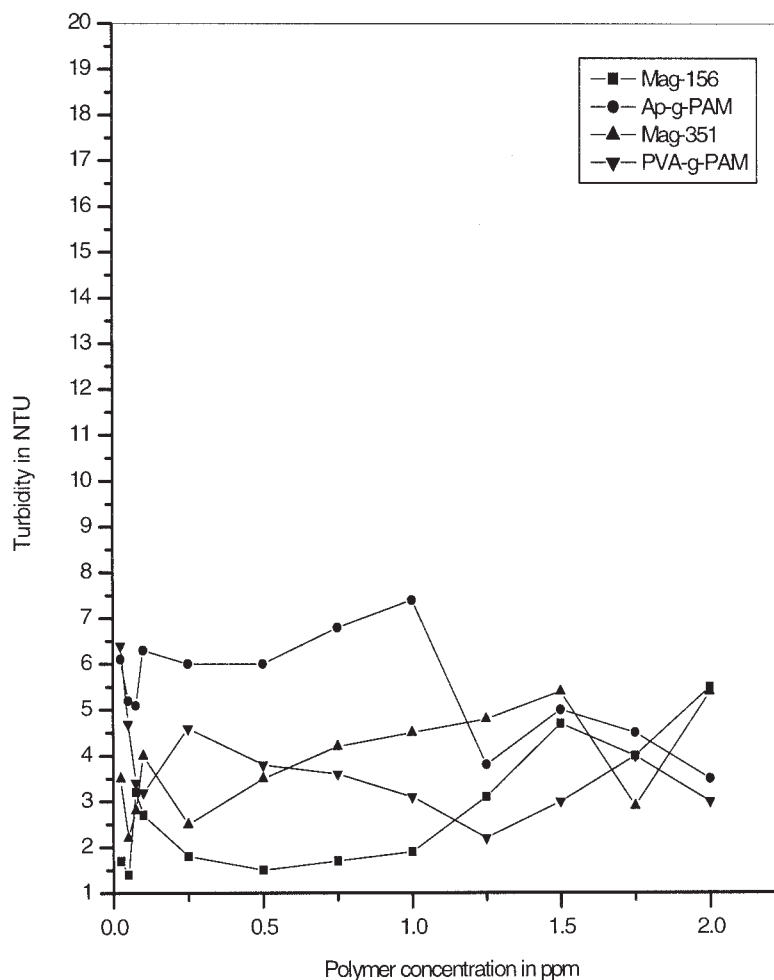


Figure 7 Flocculation performances of PVA-g-PAM and commercial flocculants in 0.25 wt % iron ore suspension.

longer the branches, the higher will be the intrinsic viscosity and vice versa. This has been observed in practice. Thus PVA-g-PAM (grade II) has a higher intrinsic viscosity (25.38) than that of others. This grade was used in all further investigations. On the basis of intrinsic viscosity results of Figure 1, it is apparent that the straightening of chains takes place in hydrolyzed PVA-g-PAM, which also increases the viscosity of the hydrolyzed PVA-g-PAM.

Alkaline hydrolysis

In hydrolyzing the graft copolymers of poly(vinyl alcohol) and polyacrylamide, the aim is to straighten the flexible polyacrylamide chains. During the treatment of PVA-g-PAM with sodium hydroxide solution, the following reactions are expected to occur: saponification of amide groups to carboxyl groups; and deetherification and depolymerization reactions of the polyacrylamide component of the graft copolymer. The extent of these reactions depends on the treatment conditions. During alkaline hydrolysis of poly(acryl-

amide) starch graft copolymer, it was shown by Khalil et al.,²⁰ that on using sodium hydroxide concentration up to 1N and temperature between 80 and 90°C, the saponification reaction (conversion of $-\text{CONH}_2$ group into $-\text{COOH}$) is the only reaction, whereas on using higher concentration of alkali, the deetherification and depolymerization reactions occur simultaneously with the saponification reaction. From Table III it is obvious that in the mentioned reaction condition, the only reaction is saponification. From the NE measurement of the partially hydrolyzed PVA-g-PAM (Table IV) it can be concluded that the carboxyl content of the hydrolyzed sample depends on potassium hydroxide concentration. The carboxyl content increases with increasing potassium hydroxide concentration.

IR spectroscopy

Evidence of grafting is provided by IR spectroscopy from Figure 2. From the IR spectra of PVA, it is obvious that PVA shows a broad peak at 3445 cm^{-1} for the

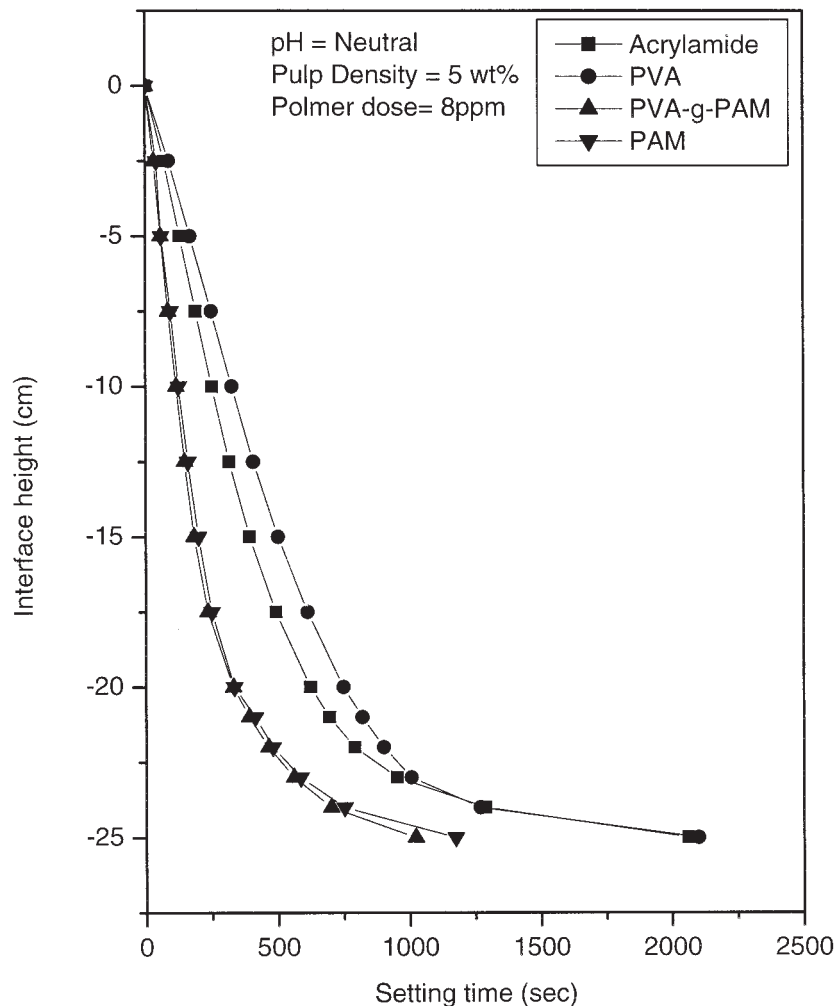


Figure 8 Settling test for 5 wt % kaolin suspension using acrylamide, polyacrylamide, PVA, and PVA-g-PAM.

-OH group, and one peak at 1065 cm^{-1} attributed to -CO groups. In the graft copolymer apart from the above peak, however, four additional peaks are present. Two peaks at 3633 and 3093 cm^{-1} are attributed to the $-\text{NH}_2$ groups (one symmetrical and the other asymmetrical stretching of two $-\text{NH}$ bonds). The peak at 1665 cm^{-1} is attributed to the amide carbonyl group and the peak at 1398 cm^{-1} is attributed to the $-\text{CN}$ group. As polyacrylamide was removed from reaction mixture, the presence of peaks at 3633 , 3093 , 1665 , and 1398 cm^{-1} in the graft copolymer provides evidence of grafting. In the hydrolyzed product, in addition to other bands, the characteristic bands of $-\text{COO}^-$ groups, one at 1512 cm^{-1} for asymmetric stretching and the other at 1406 cm^{-1} for symmetric stretching, are clearly distinguished, which is absent in the case of graft copolymer.

X-ray diffractometry

XRD analysis of poly(vinyl alcohol) shows that it exhibits a small degree of crystallinity in contrast to that

of acrylamide, which shows high crystallinity. Similarly, the result for the grafted product does not indicate crystallinity, which is indicative of the absence of acrylamide polymerization. The results are shown in the Figure 3.

Differential scanning calorimetry

Figure 4 shows the DSC curve of PVA, hydrolyzed and unhydrolyzed (best grade) PVA-g-PAM. The endothermic peaks at 124 and 124.5°C are attributed to absorbed water with respect to PVA-g-PAM and hydrolyzed PVA-g-PAM, respectively. In PVA this peak does not exist. It appears from the thermograms that the decomposition peaks in PVA-g-PAM and hydrolyzed PVA-g-PAM are at lower temperatures compared with those in PVA. Thus grafting and subsequent hydrolysis does not favor the thermal stability of PVA. The endothermic peak at 220°C is attributed to crystallization in PVA, which does not exist in PVA-g-PAM and hydrolyzed PVA-g-PAM, in conformity with XRD results.

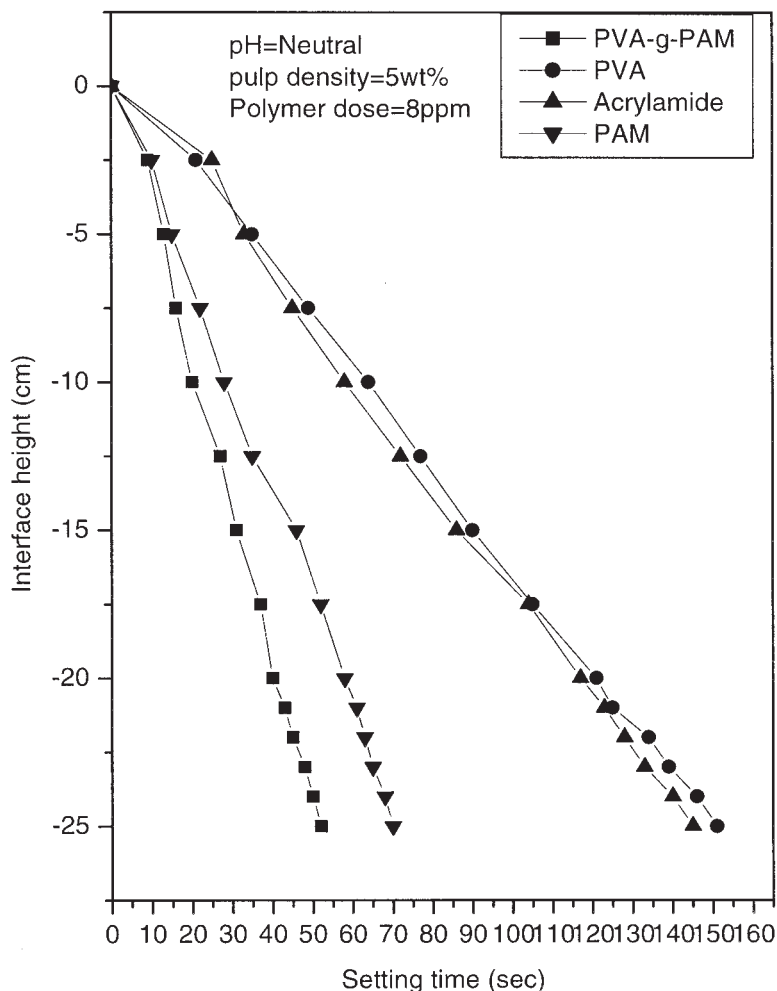


Figure 9 Settling test for 5 wt % iron ore suspension using acrylamide, polyacrylamide PVA, and PVA-g-PAM.

Rheological investigation

The plot of viscosity versus shear rate, as indicated in Figure 5, obtained from the rheometry experiment clearly shows that viscosity decreases with increasing shear rate. The following inferences can be drawn from the experimental results:

- At all shear rates, the viscosity increases for PVA transformation from its pure form to the grafted and then to grafted hydrolyzed form.
- For all three forms, an increase in shear rate decreases the viscosity, confirming the expected result from theoretical equations and exhibition of shear thinning behavior of polymer solutions.
- For transformation from pure to grafted and then to hydrolyzed grafted form, the viscosity variation becomes smoother. For the hydrolyzed form, the variation is smoothest.

Flocculation study

The major mechanisms of flocculation by polymers are charge neutralization and bridging. For neutral flocculants, flocculation is caused mainly by polymer bridging.²¹

The controversy concerning the bridging and charge-neutralization mechanisms of aggregating aqueous suspensions upon adsorption of water soluble polymers is long-standing. In the early experimental and theoretical investigations, La Mer and Hearly²² were prominent in advocating bridging. 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 onto 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 become adsorbed onto the surface 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. Thus polymers with longer chains would be more effective than those with shorter chains.

Among the three grafted products, grade II has the highest conversion efficiency and intrinsic viscosity, and thus the longer grafted polyacrylamide branches and gives the best performance among the grafted

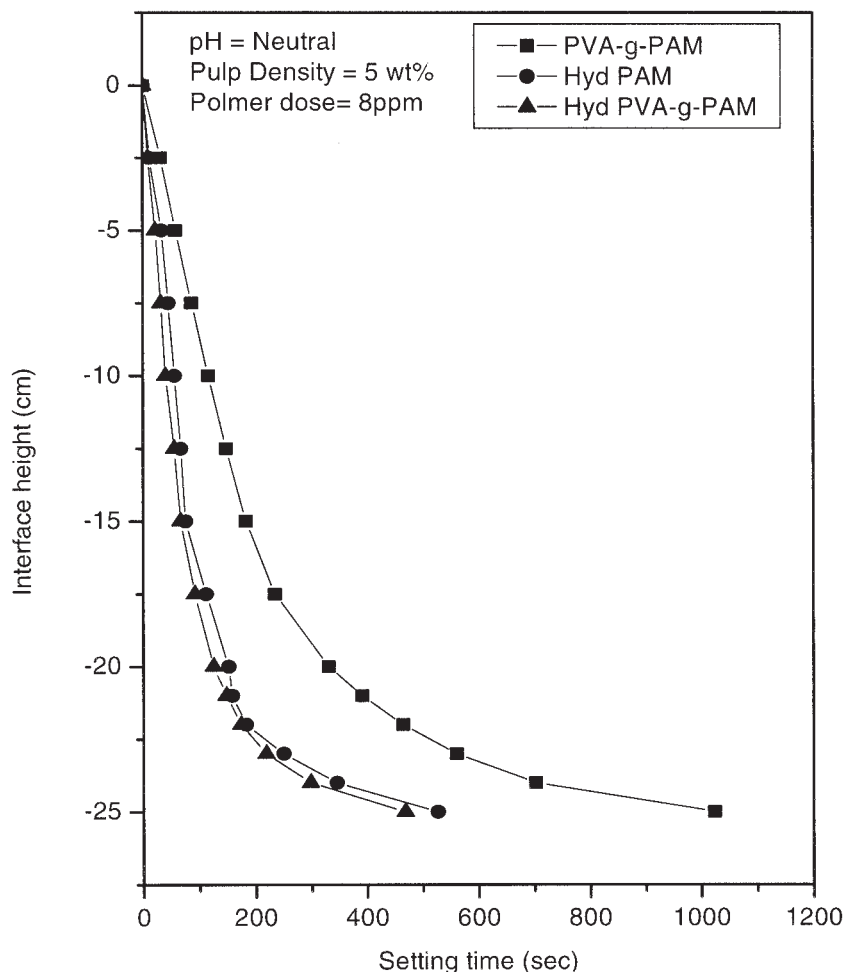


Figure 10 Settling test for 5 wt % kaolin suspension using hydrolyzed, unhydrolyzed PVA-g-PAM, and hydrolyzed PAM.

copolymers. It was used in all further experiments and is depicted as PVA-g-PAM. The flocculation efficiencies of PVA-g-PAM were tested in kaolin and iron ore suspensions. The turbidity of the supernatant liquid after flocculation was plotted against polymer concentration. Figures 6 and 7 show a comparison of the flocculation characteristics of PVA-g-PAM (grade II) with the commercial flocculants Magnafloc 351 (Mag-351), Magnafloc 156 (Mag-156), and AP-g-PAM. The turbidity results show that the PVA-g-PAM polymer shows better performance than that of Mag-156 (based on anionic PAM) and its performance is comparable to that of AP-g-PAM. Mag-351 (based on nonionic PAM) performs the best.

The settling test was carried out for iron ore and kaolin suspensions for the homopolymer (PVA), acrylamide monomer, polyacrylamide, and PVA-g-PAM at the optimum dosage (8 ppm). The grafted polymer PVA-g-PAM shows better results over that of its component monomers and polyacrylamide, as indicated in Figures 8 and 9. The flocculation performance of Hyd-II, PVA-g-PAM, and Hyd PAM in 5 wt % iron ore and kaolin suspensions is depicted in Figures 10 and 11.

The height of interface of the solid and liquid is plotted against time. The flocculation performance of a particular polymer can be correlated with settling velocity. The greater the settling velocity of the floc containing contaminants, the greater will be its flocculation performance. The result shows that the settling time for Hyd-II (468 s) is lower by 54.25% compared to that of its unhydrolyzed counterpart (1023 s) for kaolin suspension. For iron ore suspension, the reduction is 63.46%. Thus the results show a marked improvement in Hyd-II settling time performance compared to that of its unhydrolyzed PVA-g-PAM and Hyd PAM.

Upon hydrolysis, the CONH_2 group is converted to a COOH group and, as a result of electrostatic repulsion, the chain is straightened, thus increasing the flocculation efficiency. However, on the creation of more negative charges on the flocculant the repulsion between the flocculant and contaminant particles also increases, decreasing the flocculation efficiency. Thus at optimal value (Hyd-II), the straightening effect dominates and one obtains higher and optimal flocculation compared with that of ungrafted PVA-g-PAM.

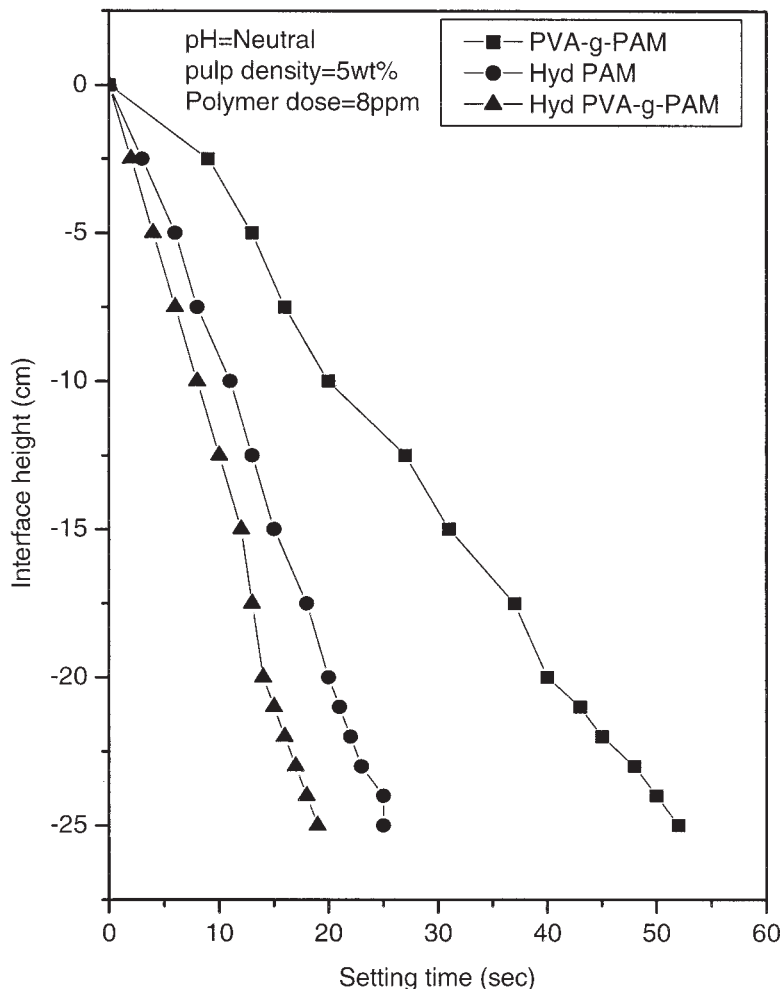


Figure 11 Settling test for 5 wt % Iron ore suspension using hydrolyzed, unhydrolyzed PVA-g-PAM, and hydrolyzed PAM.

CONCLUSIONS

From an analysis of the conducted jar test studies, it can be concluded that by grafting PAM chains onto PVA, effective flocculating agents can be developed for the treatment of wastewater. Of the grafted products, PVA-g-PAM shows better performance than that of AP-g-PAM in both suspensions. The performance of PVA-g-PAM is also better than that of other commercial flocculants. In the settling test, Hyd PVA-g-PAM shows better performance than that of unhydrolyzed PVA-g-PAM and Hyd PAM.

Through the partial alkaline hydrolysis of PVA-g-PAM, it is possible to control the carboxyl content by controlling the concentration of the alkali. It is possible to determine the neutralization equivalent (NE) of the partial hydrolyzed product by using the given formula. One product, with a certain amount of carboxyl content (NE 1000), but still having flexible grafted chains, showed better performance than that of the unhydrolyzed product. Thus by hydrolyzing the grafted poly(vinyl alcohol) to a certain extent, it is

possible to enhance the viscosity and flocculation capabilities of the virgin polymer.

References

1. Bolto, B. A. *Prog Polym Sci* 1995, 20, 987.
2. Cheremisinoff, P. N. *Handbook of Water and Wastewater Treatment Technology*; Marcel Dekker: New York, 1995; Chapter 4.
3. Lapick, L.; Alince, B.; Vande Ven, T. G. M. *J Pulp Paper Sci* 1995, 21.
4. Butler, G. B.; Angelo, R. J. *J Am Chem Soc* 1957, 73, 3128.
5. Singh, R. P.; Tripathy, T.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Pandey, S. R.; Kannan, K.; Jain, S. K.; Lan, N. T. *Curr Sci* 2000, 78, 798.
6. Deshmukh, S. R.; Sudhakar, K.; Singh, R. P. *J Appl Polym Sci* 1991, 43, 1091.
7. Deshmukh, S. R.; Singh, R. P. *J Appl Polym Sci* 1987, 33, 1963.
8. Rath, S. K.; Singh, R. P. *J Appl Polym Sci* 1997, 66, 1721.
9. Deshmukh, S. R.; Singh, R. P. *J Appl Polym Sci* 1986, 32, 6163.
10. Singh, R. P. In *Advanced Turbulent Drag Reducing and Flocculating Materials Based on Polysaccharides*; Prasad, P. N.; Mark, J. E.; Fai, T. J., Eds.; *Polymers and Other Advanced Materials: Emerging Technologies and Business Opportunities*; Plenum Press: New York, 1995; p 227.
11. Wing, R. E.; Bonae, W. M.; Russel, C. R. *J Appl Polym Sci* 1975, 19, 847.

12. Singh, R. P.; Biswal, D. R. Pat. Appl. 196/kol/2003, India, 2003.
13. Singh, R. P.; Tripathy, T.; Biswal, D. R. Pat. Appl. 101/Cal/2001, India, 2001.
14. Tripathy, T.; Singh, R. P. Eur Polym J 2000, 36, 1471.
15. Khalil, M. L.; Farag, S.; Abd El Fattah, S. J Appl Polym Sci 1995, 57, 335.
16. Mino, G.; Kaizerman, S.; Rasmussen, E. J Polym Sci 1959, 39, 523.
17. Billmeyer, F. W., Jr. Textbook of Polymer Science; Wiley: New York, 1971; p 84.
18. Morrison, R. T.; Boyd, R. N. Organic Chemistry, 6th ed.; Prentice-Hall: New Delhi, India, 1995; p 744.
19. Gregory, J. Effluent Water Treat J 1983, 23, 199.
20. Khalil, M. L.; Farag, S.; Abd El Fattah, S. J Appl Polym Sci 1995, 19, 847.
21. Gregory, J. Industrial Water Soluble Polymers; Finch, C. A., Ed.; Royal Society of Cambridge: Cambridge, UK, 1996; p 62.
22. La Mer, V. K.; Healy, T. W. Rev Pure Appl Chem 1963, 13, 112.