

Flocculation Characteristics of Grafted and Ungrafted Starch, Amylose, and Amylopectin

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ABSTRACT: Graft copolymers of starch, amylose, and amylopectin with polyacrylamide have been synthesized using a ceric-ion-initiated solution polymerization technique. In the case of amylopectin-*g*-polyacrylamide (Ap-*g*-PAM), four graft copolymers have been synthesized with variation in the number and length of grafted polyacrylamide chains. The flocculation behavior has been studied in a 0.25% kaolin suspension. It has been found that among the three graft copolymers of the starch family, Ap-*g*-PAM is the best flocculating agent compared to starch-*g*-polyacrylamide (St-*g*-PAM) and amylose-*g*-polyacrylamide (Am-*g*-PAM). Among the series of Ap-*g*-PAM, the one with fewer but longer polyacrylamide chains has been found to be the most effective flocculant. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1721–1729, 1997

Key words: starch; amylose; amylopectin; graft copolymers; flocculation

INTRODUCTION

Flocculation has played an important role in domestic and wastewater treatment, mineral beneficiation, etc.^{1–3} The flocculation is caused by addition of minute quantity of chemicals known as flocculants. The flocculants can be conveniently classified into two categories, i.e., inorganic and organic. Among the inorganic flocculants, the salts of multivalent metals, like aluminium and iron, are mostly used.⁴ The organic flocculants further fall into two categories: synthetic and natural. Synthetic flocculants are mostly water-soluble linear polymers like polyacrylamide, poly(acrylic acid), poly(diallyl dimethyl ammonium chloride) (DADMAC), poly(styrenic sulfonic acid), etc. On the other hand, starch, cellulose, alginic acid, guar gum, etc., are natural polymers that are very often used as flocculants/retention aids. Synthetic flocculants are available in all the three forms: cationic, anionic, and nonionic. Some of the

natural polymers also bear ionic groups. There are many distinct advantages offered by organic flocculants over inorganic ones. One of the most important of them is the tonnage of flocculants involved. One requires a large volume of inorganic salts to obtain the same result that can be obtained with a very small amount of polymeric flocculant. Moreover, large tonnage use of inorganic materials produces a lot of sludge, which is hardly a problem in the case of polymeric flocculants. The inorganic salts being effective over a particular pH, there is frequent need for pH adjustment. This is not a factor in the case of polymeric materials. Coming to a comparison among the latter two groups of polymers, namely, synthetic and natural polymers, one finds that synthetic polymers are much more effective than natural ones, which is due to the tailorability of the man-made polymers. It is easy to control the molecular weight, molecular weight distribution, and the nature and percentage of ionic groups on the polymeric backbone, as well as the very structure of the polymer itself. However, a great advantage of natural polymers over those of synthetic ones is probably their biodegradability and nontoxicity (the synthetic polymers themselves

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are not toxic, but the associated unreacted monomers are). At the same time, the advantage of natural polymers i.e., their biodegradability, comes as a major drawback since it reduces their storage life and tells upon their efficiency due to the lowering of the molecular weight.

It is thus evident that all the polymers, be it natural or synthetic, have one or another disadvantage. In the past, many attempts have been made to combine the best properties of both by grafting of the synthetic polymers onto natural ones. One of the great advantages thus obtained is the consequent reduced biodegradability of the grafted products because of the drastic change in the original structure of the natural polymer as well as the synthetic polymeric content in the product that is not a food for the bacteria. Moreover, it has been observed that grafting of shear degradable polymers, such as polyacrylamide onto rigid polysaccharide backbones, provides fairly shear stable systems. In the authors' laboratory, many graft copolymers have been synthesized by grafting polyacrylamide onto starch,⁵ carboxymethylcellulose (CMC),⁵ guar gum,⁶ xanthan gum,^{7,8} etc., and their shear stability, as well as drag reduction efficiencies, have been studied. Further, by variation in the number and length of grafted polyacrylamide chains onto the backbone, it has been found that the graft copolymers with fewer but longer polyacrylamide chains are more efficient as drag reducing agents. Later on, studies on flocculation behavior of such polymers followed the same trend, i.e., the graft copolymers having fewer but longer chains were found to be more effective flocculants.⁹⁻¹¹ It was postulated by one of the authors (R. P. Singh)¹¹ that graft copolymers are more effective compared to the linear polymers because of their greater approachability to the contaminants, which could be due to the spreading effect of the dangling grafted chains on the rigid polysaccharide backbone. Among grafted guar gum, xanthan gum, and starch, it has been observed that grafted starch is the most efficient flocculant.¹¹ In another study, the flocculation behavior of starch-*g*-polyacrylamide and amylose-*g*-polyacrylamide was compared.¹² The former showed better results compared to the latter. It is well known that starch consists of two polymers of anhydroglucose units: namely, amylose, the linear fraction; and amylopectin, the branched fraction. Amylose, which is the minor fraction, is of low molecular weight (in the range of 10,000–60,000),¹³ whereas amylopectin, which is the major fraction, is of high mo-

lecular weight (in the range of 50,000–10⁶).¹³ It was thus anticipated that the better efficiency of starch-*g*-polyacrylamide could be due to the larger fraction of the branched and high molecular weight amylopectin. Hence, it was planned to graft all the three polysaccharides, namely, amylose, amylopectin, and starch independently, with polyacrylamide onto each of them, and compare their flocculation efficiency with each other as well as with some of the commercially available flocculants.¹⁴ This article reports the results of this investigation in details.

MATERIALS

Amylopectin and amylose (both from corn) were purchased from Sigma Chemical Company, USA. Soluble starch and acrylamide were purchased from E. Merck, Germany. Ceric ammonium nitrate (CAN) was obtained from Loba Chemie, Bombay, India. Acetone and hydroquinone were supplied by s. d. Fine Chemicals, India. Sodium nitrate was supplied by E. Merck, Bombay, India, and kaolin by B. D. Pharmaceutical works, Howrah, India. As to the commercial flocculants, only three of them, namely, Aquaset (AS 510), Sufloc, and Ap-273 (Separan), were used for comparison. Aquaset (AS 510), which is a polyelectrolyte (the nature of charge is not known), was obtained from Aquapharm Chemical Company Private Ltd., Pune, India. Sufloc was obtained from Suyog Chemicals Ltd., Nagpur, India. The nature of Sufloc is not known. Ap-273 (Separan) was obtained from Dow Chemical Company, USA. It is a very high molecular weight polyacrylamide. All the chemicals received were used as such without further purification.

EXPERIMENTAL

Synthesis

The graft copolymers of starch, amylose, and amylopectin were synthesized by the ceric-ion-induced redox initiation method.^{15,16} The typical experimental details are as follows. 0.0154 mol (calculated on the basis of anhydroglucose units) of amylopectin was put into a conical flask with 100 cc of distilled water. The flask with a magnet in it was put on a magnetic stirrer plate. The suspension was heated to 80°C with simultaneous stirring and maintained at that temperature till

there was a distinct color change and amylopectin went into solution. It was cooled down to room temperature. Then, 0.21 mol of acrylamide was dissolved in 75 cc of distilled water and mixed with the amylopectin solution. Then the conical flask was fitted with the nitrogen inlet and outlet tubes, and oxygen-free nitrogen was purged through the solution for 20 min. At this stage, 25 cc of catalyst solution (0.22 g of CAN in 100 cc of distilled water) was added to the reaction mixture, followed by further purging with nitrogen for 10 more min. Then the nitrogen inlet tube was taken out, and the flask was sealed. The polymerization had already started by this time, which was evident from the slower motion of the magnet. The temperature showed an increasing trend, but the flask was suitably placed in a water bath to maintain the temperature at around 30°C. The reaction was allowed to continue for 24 h. At the end of the reaction, the resulting polymer was taken out into a 1 L beaker, where it was made into a homogeneous slurry with further addition of distilled water. The reaction was terminated by adding a saturated solution of hydroquinone. The viscous polymer slurry was then precipitated part by part in acetone to ensure complete precipitation. The precipitated polymer mass was kept in acetone overnight. The next day, it was transferred to a vacuum oven and dried at 70°C for about 60 h. Afterwards, it was pulverized and sieved [mesh size 52 (295 μm); test sieve BSS 410/69]. In a similar way, a series of graft copolymers using amylopectin, starch, and acrylamide were synthesized. On the other hand, the method was slightly modified in case of amylose. Since the amylose is not soluble in water, it was kept suspended in the reaction mixture with stirring and all other steps, namely, nitrogen purging, catalyst addition, etc., followed as usual. In case of amylopectin-*g*-polyacrylamide copolymers, the CAN concentration, as well as the mole of acrylamide, was suitably varied to obtain a series of graft copolymers with varying number and length of polyacrylamide chains (Ap-*g*-PAM1 to Ap-*g*-PAM4).

Viscosity Measurement

Viscosity measurements of all the polymers in solution were carried out with the help of Ubbelohde capillary viscometer (constant: 0.00527) at $27 \pm 0.1^\circ\text{C}$. A stock solution of 0.5 g/100 cc was prepared, which was further diluted with NaNO_3 solution and distilled water in such proportions that

the required concentration of polymer was obtained in 1M NaNO_3 . The time of flow was measured for solutions at five different concentrations. The low concentrations of graft copolymers were chosen in the dilution range as pointed out by Rinaudo¹⁷ for the characterization of polysaccharides. The intrinsic viscosity was obtained (from the point of intersection) after extrapolation¹⁸ of two plots, i.e., η_{sp}/C versus C , and $\ln(\eta_{\text{rel}})/C$ versus C , to zero concentration. Here C is the polymer concentration in g/100 g/dL cc; and η_{sp}/C is reduced viscosity, calculated from the relation $\eta_{\text{sp}}/C = \eta_{\text{rel}} - 1$, where $\eta_{\text{rel}} = \eta/\eta_0 \approx t/t_0$, with t being the time of flow of polymer solution and t_0 , the time of flow of solvent at the temperature of measurement. ($\ln \eta_{\text{rel}}/C$ is the inherent viscosity. One representative example is given in Figure 1, and the values of the intrinsic viscosities of all the graft copolymers are tabulated in Table I.

Flocculation

The standard Jar Test was followed. The flocculator used was supplied by M. B. Instruments, Bombay, India. The turbidity measurement was carried out with the help of the Digital Nephelo turbidity meter 132, procured from Systronics, Ahmedabad, India. 0.25% suspension of kaolin clay (prepared by dispersing 1 g of it in 400 cc of distilled water) was used for flocculation study. The suspension was taken in each of five 1 L beakers and the flocculant was added in solution form. Dose variation of flocculants was made from 0.025 to 1 ppm. The following procedure was uniformly applied for all the flocculants. Immediately after the addition of the flocculants, the suspensions were stirred at a uniform speed of 75 rpm for 2 min. This was followed by a slow stirring at 20–25 rpm for 5 min. Afterwards, a settling time of 10 min was allowed. At the end of the settling period, the turbidity of the supernatant liquids was measured by the Digital Nephelo turbidity meter. In all, 10 dose variations (0.025–1.0 ppm calculated with respect to the total weight of the solution) were made in two consecutive sets.

RESULTS AND DISCUSSION

Table I gives the details of the synthesis of the graft copolymers, i.e., the series of Ap-*g*-PAM, St-*g*-PAM, and Am-*g*-PAM. Although a number of methods are available for initiating grafting sites

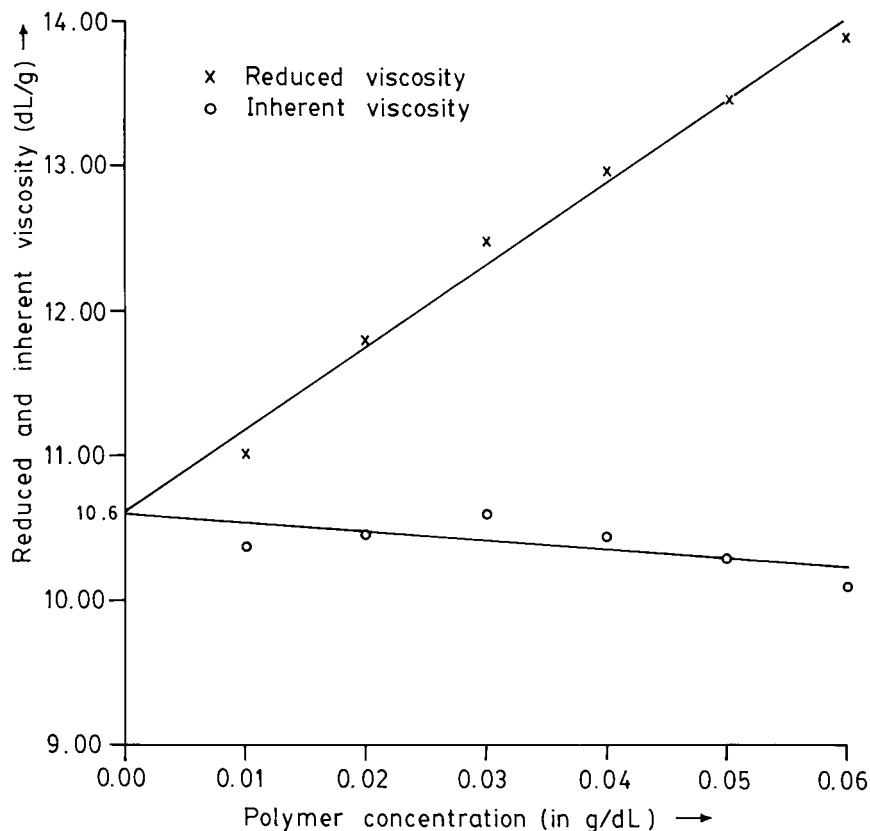


Figure 1 Plots of reduced viscosity versus concentration and inherent viscosity versus concentration in the case of Ap-g-PAM1.

on a polysaccharide backbone,^{16,20} the ceric-ion-induced redox initiation method¹⁵ has been preferred to most of them over the years. It is because of the fact that the redox process initiates free radical sites^{21,22} exclusively on the polysaccharide backbone, thus providing little scope for homopolymer formation. Deshmukh⁵⁻⁸ has proved the absence of homopolymer in the following manner.

Two sets of polymerization reactions were carried out. In one set, CAN was added to acrylamide with all other usual procedure, except that starch was not added to the reaction mixture deliberately. In the other set, the reaction was carried out as usual in the presence of polysaccharide. As expected, the reaction did not take place in the first case, thus indicating that the presence of the

Table I Details of Synthesis of the Graft Copolymers

No.	Polymer	Polysaccharide (mol AGU) ^a	Acrylamide (mol)	Amount of CAN (mol × 10 ⁴)	Conversion (%) ^b	Intrinsic Viscosity (η , dL/g)
I	Ap-g-PAM 1	0.0154	0.21	1.003	87.6	10.6
II	Ap-g-PAM 2	0.0154	0.21	2.006	90.95	7.0
III	Ap-g-PAM 3	0.0154	0.28	1.003	77.8	9.55
IV	Ap-g-PAM 4	0.0154	0.14	1.003	84.1	7.46
V	St-g-PAM	0.0154	0.14	1.003	89.33	6.86
VI	Am-g-PAM	0.0154	0.14	1.003	72.38	7.5

^a Calculated on the basis of anhydroglucose units (1 g mol of AGU is equal to 162 g).

^b Percentage of conversion is calculated from the following relation¹⁹: conversion = [(weight of graft copolymer - weight of polysaccharide)/amount of acrylamide] × 100.

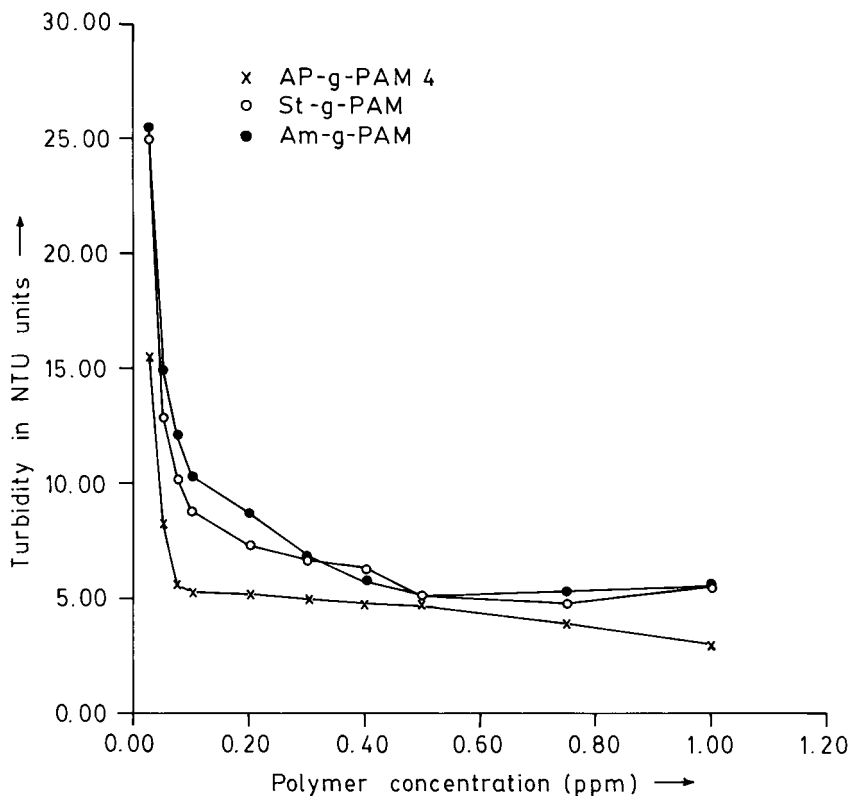


Figure 2 Variation of supernatant turbidity with flocculant dose in kaolin suspension (0.25%) in water. The comparison is among Ap-g-PAM4, St-g-PAM, and Am-g-PAM.

polysaccharide is essential for the creation of free radical sites, which further initiated the process of graft copolymerization. Proof of grafting has also been obtained from rheological investigations.²³ It is known that polysaccharides that have rigid backbones are shear stable, whereas synthetic polymers like polyacrylamide are shear degradable. Thus, a graft copolymer of the above two should be fairly more shear stable than that of pure polyacrylamide. Ungeheur et al.²³ have shown that graft copolymer of xanthan gum and polyacrylamide show much improved shear stability (almost of the same order as that of the polysaccharide itself) compared to polyacrylamide. This proves that the polyacrylamide chains are attached to the polysaccharide backbone and are not isolated ones. They have also shown that the mixture of xanthan gum and polyacrylamide, having their proportion equivalent to that present in graft copolymer, have much lower shear stability than the graft copolymer. Further proof of grafting and absence of homopolymerization is available from the studies of Owen and Shen.²⁴ They observed that high concentration of acrylamide

always resulted in homopolymerization; but acrylamide concentration of less than 2.0M, nitric acid concentration of less than 1.2M, and CAN concentration of less than 0.1M resulted in absence of homopolymerization.

In synthesizing the series of graft copolymers involving amylopectin and polyacrylamide, the aim was to have a number of graft copolymers with varying number and length of polyacrylamide chains. As is well known,²⁵ amylopectin itself has a branched structure. This makes it to attain a somewhat compact shape in solution, resulting in lower intrinsic viscosity due to the smaller hydrodynamic volume of the solvated polymer molecules. As we go on, grafting polyacrylamide onto it, two changes are possible. One can either have a small number of long polyacrylamide chains or a large number of short polyacrylamide chains in the graft copolymer. In the former case, the compact shape of the original amylopectin would be changed due to the presence of long polyacrylamide chains. This would result in larger hydrodynamic volume, leading to higher intrinsic viscosity. On the other hand, a large

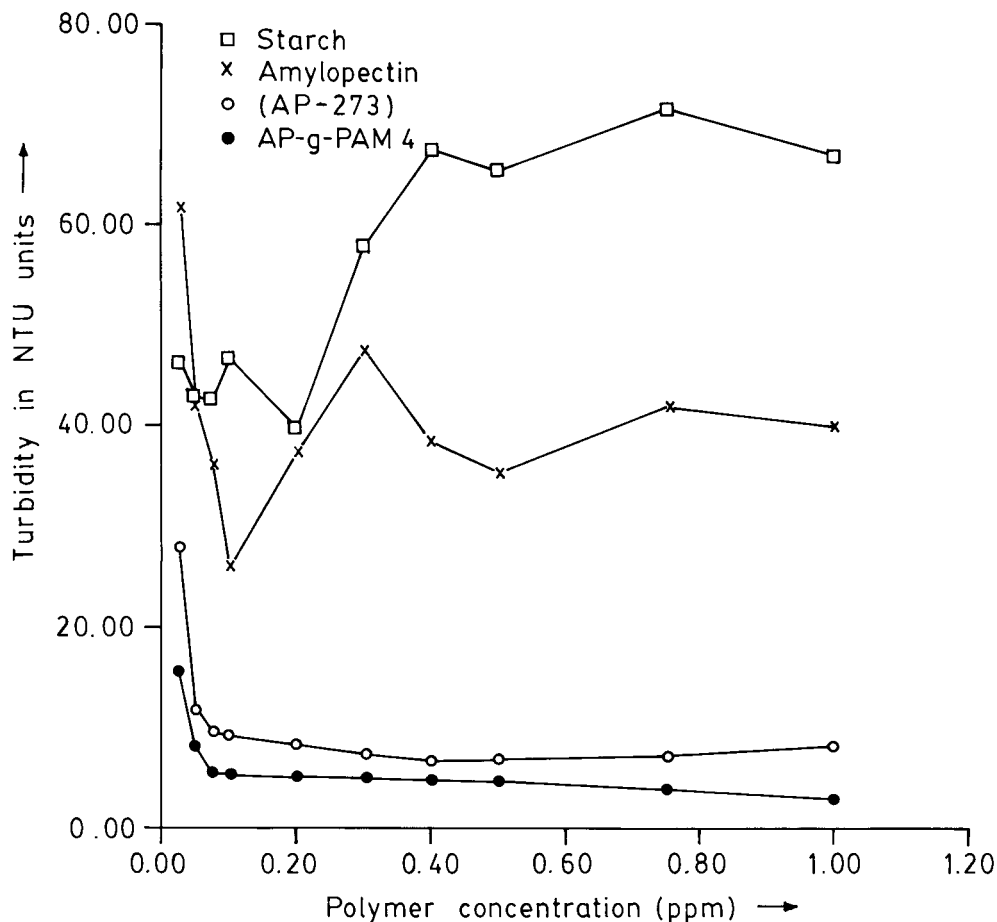


Figure 3 Variation of supernatant turbidity with flocculant dose in kaolin suspension (0.25%) in water. The comparison is among starch, amylopectin, Ap-273, and Ap-g-PAM4.

number of short polyacrylamide chains will not alter the original compact shape to a great extent, thus retaining its lower hydrodynamic volume, which should be reflected again in its low intrinsic viscosity. Comparing the four graft copolymers in Table I above, we see the drastic change in the intrinsic viscosity between Ap-g-PAM1 and Ap-g-PAM2. The CAN concentration in case of Ap-g-PAM2 was deliberately doubled to reduce the length of polyacrylamide chains since a greater number of free radical sites (created by the higher concentration of CAN) will have to compete for the same monomer concentration. It is a fact that the intrinsic viscosity of a polymer, although greatly dependent on its molecular weight, is also significantly influenced by the structure of the polymer in solution.²⁵ The intrinsic viscosity value, which is a measure of the hydrodynamic volume of the polymer in solution, is lower for a branched polymer in comparison to a linear poly-

mer of approximately same molecular weight. Thus, in the case of a series of graft copolymers with the same backbone, the longer the grafted chains, the higher the hydrodynamic volume and, hence, the intrinsic viscosity. This has been observed in practice. Similarly, comparing Ap-g-PAM1 with Ap-g-PAM4, we observe a sharp fall in intrinsic viscosity. This is again due to the shorter length of polyacrylamide chains, which results at lower acrylamide concentration, keeping the CAN concentration fixed. On the other hand, when we compare Ap-g-PAM3 with the other graft copolymers in the series, e.g., with Ap-g-PAM1, we expect an increase in the intrinsic viscosity, which should have been, given the higher concentration of acrylamide at the same CAN concentration. However, the intrinsic viscosity shows a downward trend due to the lower monomer conversion in this case (Table I).

The results of the flocculation study have been

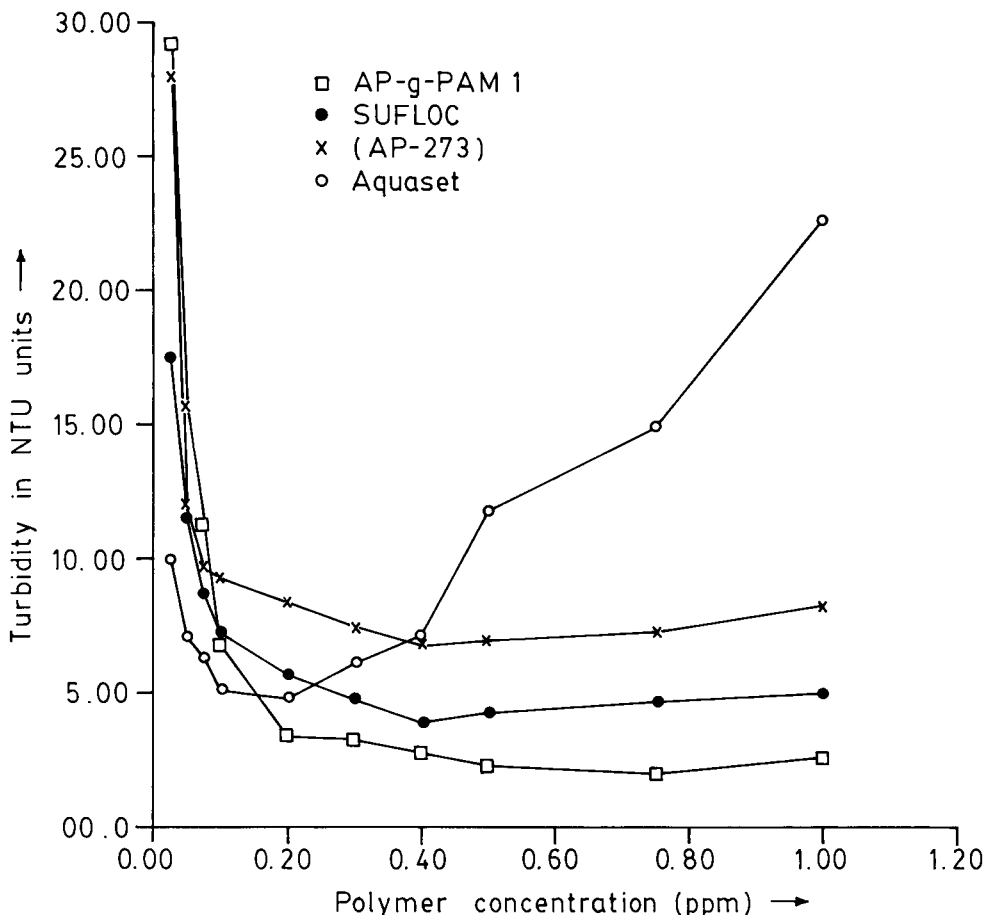


Figure 4 Variation of supernatant turbidity with flocculant dose in kaolin suspension (0.25%) in water. The comparison is among Ap-g-PAM1, Sufloc, Ap-273, and Aquaset.

shown in Figures 2–5. In each case, the turbidity of supernatant liquids after flocculation has been plotted against polymer concentration. Figure 2 compares the turbidity versus polymer concentration in the case of three graft copolymers, namely, Ap-g-PAM4, St-g-PAM and Am-g-PAM. Here, Ap-g-PAM4 was deliberately chosen from among the four graft copolymers because it has the same ratio of acrylamide to amylopectin and at the same catalyst concentration (compared to the other two graft copolymers chosen). Hence, this is supposed to have approximately the same number and length of polyacrylamide chains. As observed in Figure 2, Ap-g-PAM4 has shown better performance compared to the other two graft copolymers. On the other hand, there seems not to be much of a difference between Am-g-PAM and St-g-PAM at the extreme ends of the polymer doses used; but in the range of 0.05–0.3 ppm, the performance of St-g-PAM clearly outweighs that of Am-g-PAM. At higher doses, the effect of deflocculation starts manifesting.

In Figure 3, the efficiency of Ap-g-PAM4 has been compared with starch, amylopectin, and Ap-273. The behavior of amylose could not be studied because of its insolubility in water. In cases of starch and amylopectin, there was practically no floc formation, which may be the reason for the zigzag behavior in their curves. On the other hand, Ap-g-PAM4 is much more efficient compared to Ap-273.

Figure 4 compares the efficiency of four graft copolymers, namely, Aquaset (AS 510), Ap-273 (Separon), Sufloc, and Ap-g-PAM1. The Ap-g-PAM1 has been deliberately chosen because it has longest side chains among all the graft copolymers. Again, here as well, the graft copolymer dominates the commercial flocculants in terms of its flocculation efficiency and consequent lower supernatant turbidity of the solution. It may be noted that Aquaset, which works appreciably at lower doses, shows an upward trend at higher doses. Ap-g-PAM1, Ap-273, and Sufloc do not show any upward trend until the highest dose of

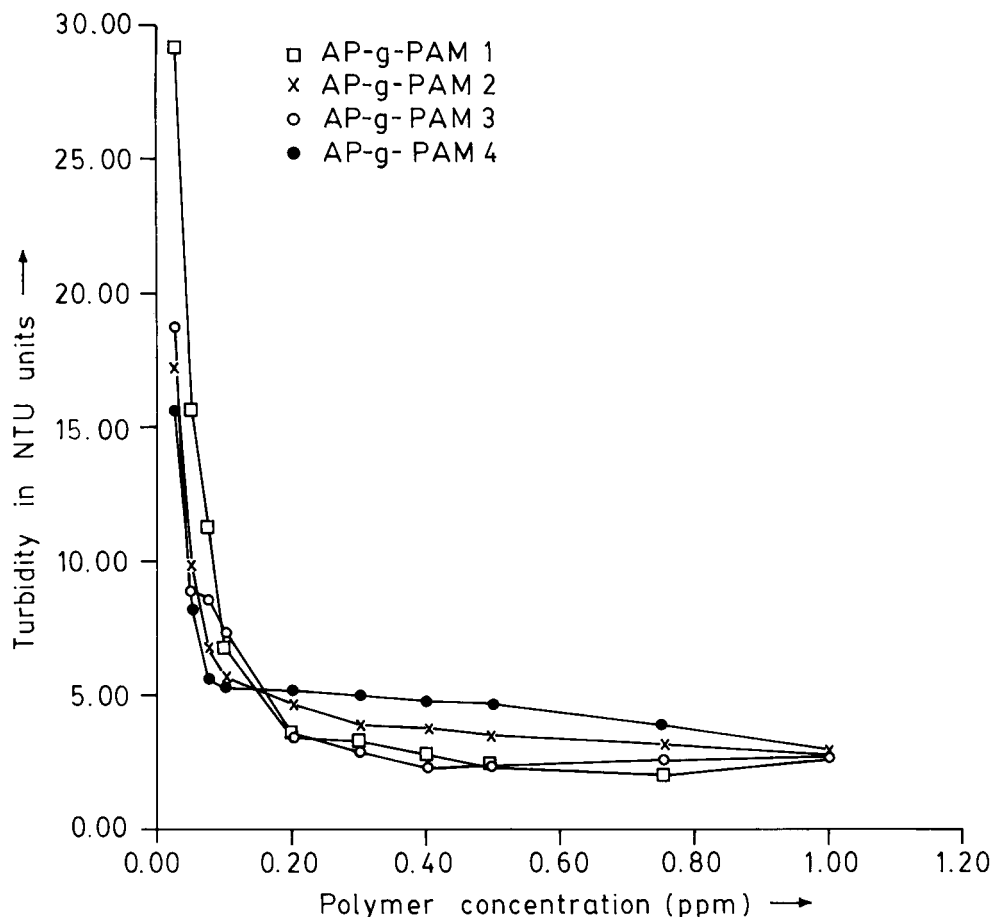


Figure 5 Variation of supernatant turbidity with flocculant dose in kaolin suspension (0.25%) in water. The comparison is among the four graft copolymers of amylopectin and polyacrylamide.

polymer, i.e., 1 ppm; but Ap-*g*-PAM1 is definitely the best among the four flocculants, as observed from the plots. This vindicates the earlier observation¹¹ that a graft copolymer is more efficient as a flocculant than a linear polymer. Lastly, the series of graft copolymers of amylopectin and polyacrylamide have been compared among themselves in Figure 5. The trend is especially clear in the range of 0.2–2.0 ppm polymer dose. Among the three graft copolymers, namely, Ap-*g*-PAM1, Ap-*g*-PAM2, and Ap-*g*-PAM4, the one with fewer but longer polyacrylamide chains, i.e., Ap-*g*-PAM1 (please see Table I), shows the best result among the three.

CONCLUSION

It may be concluded on the basis of the above investigation that Ap-*g*-PAM is the best floccu-

lating agent compared to St-*g*-PAM and Am-*g*-PAM. The enhanced efficiency of Ap-*g*-PAM is because of its greater degree of branching and higher molecular weight. The synthesis parameters influencing the number and length of polyacrylamide chains have a direct bearing on the flocculation characteristics of the graft copolymers. Thus Ap-*g*-PAM1, which is the one with fewer but longer grafted polyacrylamide chains, is the best in the series.

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