

Biodegradable Flocculants Based on Partially Hydrolysed Starch-g-Polyacrylamide

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ABSTRACT

Partial hydrolysis of the Starch-g-Polyacrylamide was carried out in alkaline medium. Three grades of partially hydrolysed products were synthesized by varying the reaction parameters. The neutralization equivalent of these products was determined by titrating with standard NaOH solution. Flocculation characteristics of all the hydrolysed graft copolymers were determined in 0.25wt% silica suspension. The partially hydrolysed product with higher neutralization equivalent (Hyd St 3) shows better performance than other partially hydrolysed as well as unhydrolysed products in flocculation. The flocculation performance of Hyd St 3 was also compared with four commercially available flocculants Mag.156, Mag.155, Mag.351 and Rish 440 HV in 5 wt% iron ore and 0.25wt% of silica suspension. The flocculation performance of Hyd St 3 was also compared with Starch-g-polyacrylamide (St-g-PAM) and Starch in 0.25wt% silica suspension. The results show that the flocculation performance of Starch-g-polyacrylamide is enhanced after partial alkaline hydrolysis and the performance of Hyd St 3 is at per of some commercial flocculants and is also better of some other commercial flocculants.

1. Introduction

Flocculation is a process [1] that involves the formation of aggregates and the settling of colloidal particles from stable suspensions caused by the addition of soluble chemicals known as flocculants in the minute quantities. Polymeric flocculants are extensively used for treatment of industrial effluents and mineral processing [2,3]. High molecular weight synthetic polymers like polyacrylamides are very effective flocculating agents. However these polymers are unstable in shear fields and hence lose their flocculation effectiveness. The natural polymers like polysaccharides exhibit good

resistance to shear degradation. However, they are less effective flocculating agents when compared with synthetic polymers and their aqueous solutions are also susceptible towards biodegradation. Singh et al.[4] have synthesized graft copolymers of acrylamide with various natural polysaccharides. It has been found that [5] the graft copolymers of polysaccharides and polyacrylamide exhibit much better flocculation characteristics than the conventional polysaccharide and synthetic polymer based flocculants. It was also pointed out that [5] the enhanced flocculation characteristics are due to the ease in approach of flexible polyacrylamide chains grafted into rigid polysaccharide backbones to the contaminant particles in the effluents.

It has been observed in some cases that partially hydrolysed polyacrylamide shows better flocculating behaviour than polyacrylamide itself [6,7]. These polymers are generally prepared by treatment of alkali. With hydrolysis, the polyacrylamide acquires a polyelectrolyte character. As a result the viscosity of the polymer solution increases due to coil expansion. This enhances their flocculation characteristics. The present paper reports the synthetic details of partially hydrolysed starch-g-polyacrylamide (St-g-PAM) and its flocculation performance in 0.25wt% silica and 5wt% iron ore suspensions. The objective of partial hydrolysis of the grafted St-g-PAM was to establish the relation between the flocculation efficiency with expansion and straightening of the grafted flexible PAM chains. As a result of hydrolysis the CONH₂ groups of PAM chains are converted to the -COO⁻ groups. As a result, two adjacent negatively charged group repel each other, so the chains will be expanded and straightened.

2. Experimental

2.1 Materials

Starch and Ceric ammonium nitrate (CAN) was procured from Loba Chemie, Bombay India. Acrylamide was procured from E-Merck, Germany. Acetone and ethanol was procured from s.d.Fine Chem.Ltd. Bombay,India. Sodium hydroxide was procured from E.Merck, Bombay, India. Magnafloc 156, Magnafloc 155, Magnafloc 351 are procured from Ciba Specialty Chemicals Ltd., England and Rishfloc 440 HV is purchased from Rishabh Metals & Chemicals (P) Ltd., Mumbai, India.

2.2 Synthesis of Starch-g-Polyacrylamide (St-g-PAM)

The method of preparation of Starch-g-PAM, the procedure for intrinsic viscosity measurement and for the calculation of % conversion is given in the previous report [8]. The Synthetic details are given in Table -1.

Table. 1 : Synthetic details of Starch-g-Polyacrylamide

Starch (gm)	Acrylamide (Mol)	Amount of CAN (Mol $\times 10^4$)	% Conversion	Intrinsic Viscosity (dl/gm)
2	0.12	3.009	88.48	6.68

2.3 Alkaline hydrolysis of St-g-PAM

Alkaline hydrolysis of St-g-PAM was performed as follows: 2 gm of St-g-PAM was dissolved in 200cc of distilled water then the required amount of NaOH was added to it. This mixture was placed in a thermostated water bath at specified temperature. At the end of the required reaction time the content of the flask was poured into 400 ml of ethyl alcohol. The product was filtered and washed with an ethanol: water mixture (70:30 by volume) and finally with ethanol. It was then dried. Three hydrolysed products are obtained by varying the reaction conditions. The results are shown in Table -2. The hydrolysed products are referred to as Hyd St 1, Hyd St 2 and Hyd St 3.

Table 2: Synthetic details of partial alkaline hydrolysis of St-g-PAM

Polymer	Amount of St-g-PAM (gm)	Volume of 1 (N) NaOH	Reaction Temperature ($^{\circ}$ C)	Reaction time (hours)
Hyd St 1	2	25	50	1
Hyd St 2	2	50	50	1
Hyd St 3	2	100	50	1

2.4 Determination of neutralization equivalent (N.E.) of the hydrolysed polymer

Neutralization equivalent (N.E.) is the equivalent weight of the acid, is determined by titration with standard base [9]. Neutralization equivalent of an acid can be determined in the following way.

Let x gm of sample of an unknown polybasic acid sample require y ml of z (N) NaOH for complete neutralization. Since 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.

$$(y \times z) / 1000 \text{ equivalent acid} = x \text{ gm.}$$

$$1 \text{ equivalent acid} = (x \times 1000) / (y \times z)$$

Thus the equivalent weight of the acid will be equal to: $(x \times 1000) / (y \times z)$

0.5 gm of each hydrolysed polymers was dissolved in 150 ml of distilled water in a conical flask. After that 40 cc 0.1012 (N) HCl was added to each of the three solutions. The flasks were kept for 6 hours under this condition. Then the solutions are back titrated with standard 0.1074 (N) NaOH to neutralize the excess HCl. During alkaline Hydrolysis $-\text{COONa}$ groups are generated. To generate the $-\text{COOH}$ groups, HCl was added to the

mixture. Since HCl is much stronger than organic acid it will be neutralized. Organic acids are not dissociated in presence of HCl due to common ion effect. 40 cc 0.1012 (N) HCl was titrated by 0.1074 (N) NaOH solution. The difference between the titre value of only HCl and the excess HCl in polymer solutions gives the volume of alkali required for titrating the acid formed during acidification of the polymer. The N.E. value of polymers are given in Table 3.

Table 3: Determination of Neutralization Equivalent (N.E.)

Sample	Volume of 0.1074(N) NaOH (V_2) cc	($V_1 - V_2$) ^a (cc)	N.E. (gm)
Hyd St 1	37.4	0.3	6207
Hyd St 2	36.95	0.75	2483
Hyd St 3	36.25	1.45	1284

^a V_1 is the volume of 0.1074 (N) NaOH to neutralize 40 cc of HCl = 37.7 cc

2.5 Flocculation studies

A standard Jar test procedure was followed [10] for the flocculation study of 0.25wt% silica suspension and for the flocculation study of the iron ore suspension (5wt %) column test is used [11]. The flocculator used was supplied by MB Instruments, Bombay, India. Turbidity measurements were carried out using Digital Nephelo Turbidity meter 132, procured from Systronics, Ahmedabad, India. The results are shown in Fig. 1, Fig. 2 and Fig. 3.

3. Results and discussions

In hydrolyzing the graft copolymers of starch and polyacrylamide the aim was to straighten and expand the flexible polyacrylamide chains. The extent of hydrolysis depends on the treatment conditions. From the NE measurements of the partially hydrolysed St-g-PAM and unhydrolysed St-g-PAM it can be concluded that the carboxyl content of the hydrolysed samples depends on the NaOH concentration. The carboxyl content increased on increasing the concentration of NaOH. NE gradually decreases from the hydrolysed products 1-3. NE values indicate the number of basicity of a polybasic acid. NE is equal to molecular weight of the acid/basicity. During alkaline hydrolysis of the amide groups molecular weight of the polymer would remain same. Hence the greater number of carboxyl groups (basicity) lower will be the NE value.

The flocculation performance of three partial hydrolysed products namely Hyd St 1, Hyd St 2, Hyd St 3 in 0.25 wt% silica suspension is depicted in Fig. 1. From Fig. 1, it is obvious that with increasing carboxyl content of the hydrolysed graft copolymer the flocculation

performance increases. Hyd St 3 with greater carboxyl content shows better performance. During hydrolysis the PAM chains get straightened and expanded a little bit hence approach to the contaminant particles becomes easier. Similar result (Fig. 3) is also obtained when the flocculation performance of Hyd St 3 is compared with St-g-PAM and Starch (St) in 0.25 wt% silica suspension. Here also Hyd St 3 shows better performance than that of Starch (St) and St-g-PAM.

In Fig. 3 the flocculation performance of Hyd St 3 is compared with some commercially available flocculants namely Magnafloc-156 (Mag.156), Magnafloc -155 (Mag.155), Magnafloc-351(Mag.351) and Rishfloc -440 HV (Rish. 440 HV) in 0.25 wt% silica suspension. The commercially available flocculants are mainly polyacrylamide based linear polymers. Their structures and compositions are totally classified by their manufacturers. Since they are also polyacrylamide based, they are taken for the comparison. From the fig it is also obvious that the performance of Hyd St 3 shows better performance than Magnafloc-156 and Rishfloc 440 (HV).

In Fig. 4 ; the flocculation performance of Hyd St 3 is compared with Magnafloc -156, Magnafloc-155, Magnafloc-351 and Rishfloc-440 HV in 5 wt% iron ore suspension. In this figure, the height of interface between 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. Here the flocculation performance of Hyd st 3 is at par with some commercially available flocculants.

4. Conclusion

From the above study it can be concluded that during partial alkaline hydrolysis Starch-g-Polyacrylamide, it is possible to control the carboxyl content by controlling the reaction parameters. It is possible to determine the neutralization equivalent of the partial hydrolysed product by using the given formula. One product, with a certain amount of carboxyl content (NE = 1284 gm) showed better performance than the unhydrolysed product. Hence by partial hydrolysing the grafted starch to a certain extent, it is possible to enhance the flocculation capabilities of the virgin polymer.

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REFERENCES

1. Bratby, J. Coagulation and Flocculation, Uplands Press, Croydon, England, (1980)
2. Gregory, J. Polymer Flocculation in Flowing Dispersions, in : The effect of Polymers on Dispersion properties, T.F. Tadros (Ed). London Academic Press, (1982)
3. Tripathy, Tridib, Karmakar, N.C., Singh R.P., JAPS, 82, 375, (2001).
4. Singh, R.P., Tripathy, T. Karmakar, G.P., Rath, S.K., Karmakar, N.C., Pandey, S.R. Kannan, K., Jain, S.K. and Lan, N.T., Novel Biodegradable Flocculants Based on Polysaccharides, Current Science, 78 (7), 798, (2000).
5. Singh R.P., Advanced Turbulant Drag Reducing and Flocculating Materials Based on Polysaccharides”, In: Polymers and Other Advanced Materials; Emerging Technologies and Business Opportunities, P.N. Prasad. J.E. Mark and T.J. FAi Eds. Plenum Press, New York, London, 227, (1995)
6. Wing R.E., Bonae, W.M., C.R. Russel, JAPS, 19, 847, (1975)
7. Tripathy Tridib, Singh, R.P., European Polymer Journal, 36, 147, (2000)
8. Tripathy, T., Pandey, S.R., Karmakar, N.C., Bhagat, R.P., Singh, R.P. European Polymer Journal, 35, 2057, (1999).
9. Morrison R.T., Boyd, R.N., Organic Chemistry, 6th Ed., Prentice-Hall Inc., Publishers, 744, (1995)
10. Tripathy, Tridib, Bhagat, R.P. , Singh, R.P., European Polymer Journal, 37, 125, (2001)
11. Pandey S.R., Tripathy, T., Bhagat R.P., Singh, R.P., Macromolecules, New Frontiers, K.S.V. Srinivasan Ed., Allied Publishers, New Delhi, 2, 1114, (1998).

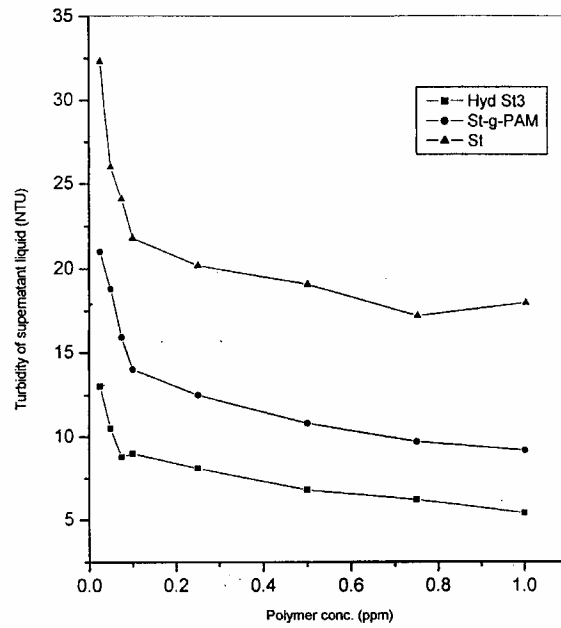


Fig 1 : Jar test result in silica suspension (0.25 wt%) using Hyd St1-Hyd St3 as flocculants.

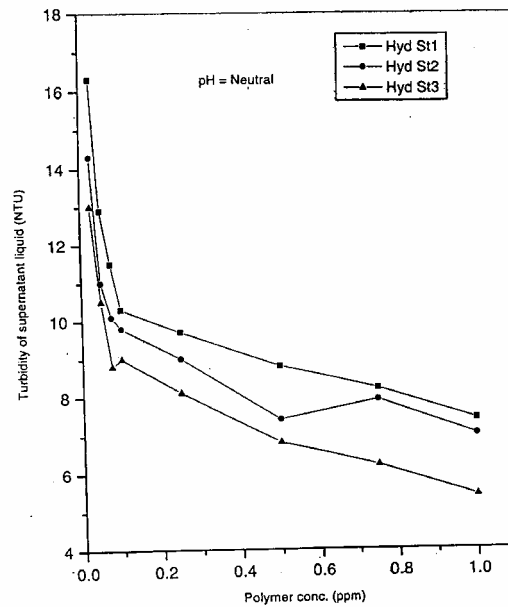


Fig 2 : Jar test result in silica suspension (0.25 wt%) using St, St-g-PAM and Hyd St3 as flocculants.

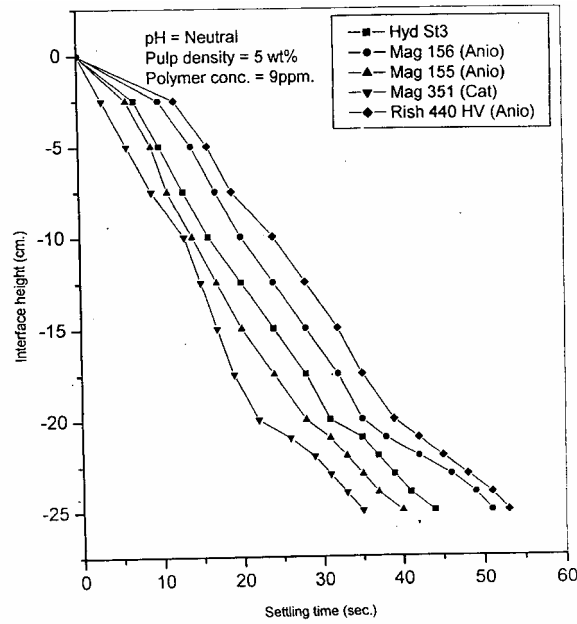


Fig 3 : Jar test result in silica suspension (0.25 wt%) using Hyd St3 and commercial flocculants.

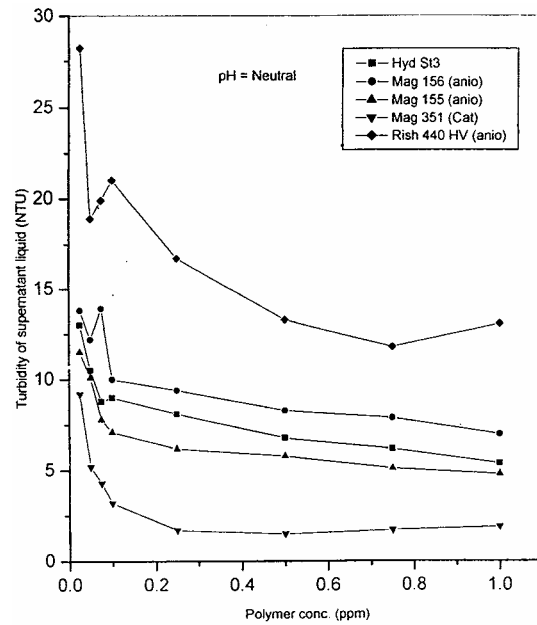


Fig 4 : Settling test results in iron ore suspension using Hyd St3 and commercial flocculants.