Novel Polymeric Flocculants Based on Polyacrylamide Grafted Dextran in Kaolin Suspension

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ABSTRACT: A study is done on ceric-ammonium-nitrate (CAN) initiated graft copolymerization of polyacrylamide (PAM) on to dextran (Dx) by solution polymerization technique. The average molecular weight of dextran is 7.0×10^{-6} g/mole. By changing the concentrations of the initiator in the reaction feed, a series of graft copolymer (Dx-g-PAM1 to Dx-g-PAM4) with variation in the number and length of the grafted PAM chains are obtained. The flocculation characteristics of various polymers are investigated by the use of settling tests in 2 wt % using kaolin suspensions. Among the series of graft copolymers, the one with highest molecular weight shows superior performance. The flocculation characteristics of the best-performing graft copolymer (Dx-g-PAM3) are compared with those of various commercially available flocculants and PAM in the kaolin suspension. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3539–3544, 2010

Key words: dextran; flocculation; graft copolymer; solution polymerization

INTRODUCTION

The commercially important dextran is produced from sugar beet sucrose, which is fermented by bacterium leuconostoc mesenteroids- B512F and contains mainly α-D-(1–6) linked units (95%) and α-D-(1–3) linked branch units (5%). The average molecular weight of dextran is 7×10^6 (Dx). Dextran is water soluble, biodegradable, and versatile polysaccharide used extensively in the waste-water treatment (flocculation), pharmaceutical industry, photographic, cosmetic, and agricultural industries.

Water-soluble polymers represent a major class of polymers comprising of biopolymers and synthetic macromolecules. Biopolymers consist of nucleic acids, proteins, and polysaccharides. Synthetic water-soluble polymers comprise a large group of commercially useful products, such as poly (acrylamide), poly (vinyl alcohol), poly (ethylene glycol), poly (acrylic acid), etc. Most applications of synthetic water-soluble polymers depend mainly on their flocculation and surface-active properties. As a result, water-soluble polymers find uses in many areas ranging from food additives to flocculating agents.

Among the natural and synthetic polymers used for application in flocculation,[1] synthetic polymers are much more effective than natural polymers, which is attributed to the easy tailorability of the man made polymers. It is well known that polyacrylamide and its copolymers are used as good flocculants for the beneficiation of mineral and paper industry. The serious drawback of polyacrylamide lies in the fact that it is degraded by shear forces. The advantage of natural polymers over synthetic ones is their low cost, non-toxicity, biodegradability, and shear resistance characteristics.[2] The biodegradability of natural polymers comes as a drawback in that it reduces the storage life and performance.

Grafting is an important procedure to obtain suitably modified polymers, which combines the properties of both natural and synthetic polymers. The great advantages thus obtained are high flocculation efficiency, controlled biodegradation, vicosifying and shear resistance characteristics of the developed graft copolymers.[3] Various types of graft copolymers have been synthesized by grafting polyacrylamide (PAM) onto the polysaccharides[4–8] backbone. It has been observed that these graft copolymers show significant increase in viscosity at all shear rates. This is due to the longer PAM chains grafted to the polysaccharides.

Flocculation is a process of bringing together small particles to form large particles (flocs), often highly porous in nature. Whereas coagulation of colloidal dispersions by addition of electrolyte such as alum, calcium, and iron salts, etc., generally yields coagulants of small sediment volume than larger volumes and exhibit greatly enhanced filtration rates. Among polymeric flocculants, the synthetic polymers can be

tailor made by controlling molecular weight, molecular weight distribution, the structure of polymers and the nature and percentage of ionic groups. Thus the synthetic polymers are very efficient flocculants.[9–11]

This paper is focused on the flocculation studies (Settling test) of various grades of graft copolymers based on polyacrylamide and dextran obtained by varying initiator (CAN) concentrations.

MATERIALS

Dextran is procured from Sigma Chemicals. Acrylamide is procured from E. Merck, Germany. CAN is obtained from Loba Chemie, Mumbai, India. Acetone and hydroquinone are supplied by S.D Fine Chemicals, Mumbai, India. Nitric acid is obtained from E.Merck, Mumbai, India. The source and chemical nature of the commercial flocculants are given in Table I. Kaolin is obtained from C. D. Pharmaceutical, Howra, India. Particle size, chemical composition, and zeta potential of kaolin are given in Table II.

EXPERIMENTAL

Synthesis

The graft copolymers are synthesized by ceric ion / HNO_3 induced redox initiation method using solution polymerization technique. The graft copolymers are treated with a mixture of acetic acid and formamide (1 : 1 by volume) to remove the homopolymer polyacrylamide. Four grades of graft copolymers are synthesized with different concentration of initiator. The details of synthetic procedure are given elsewhere.[12,13] Synthesis of polyacrylamide is achieved using the same experimental conditions as used for synthetic graft copolymer.

Intrinsic viscosity measurements

Viscosity measurements of the aqueous solution of the graft copolymers (Dx-g-PAM1 to Dx-g-PAM4) are carried out with the help of Ubbelohde viscometer (P/2741). The viscosities were measured in a constant temperature bath (digital-control water bath, Thermo fisher, UK) maintained at $25 \pm 0.1°C$. A 0.1 g sample of the polymer was dissolved in distilled water and the volume was made up to 100 cc. From the time of flow of pure solvent (t_0, for distilled water) and the polymer solutions (t), relative viscosity ($\eta_r = t/t_0$) was obtained. The terms related to viscosity measurements are given as follows: specific viscosity η_r-1 = η_{sp}; reduced viscosity η_{sp}/C = red; inherent viscosity $\ln\eta_r/C$ = η_{inh}; and intrinsic viscosity = $(\ln\eta_{sp}/C)_{c=0}$ =[η].

Calculation of approximate molecular weight

The percentage of polysaccharides is small in comparison with the polyacrylamide. Hence, in case of the grafted polysaccharides, several workers[14,15] have used the Mark Houwink equation for PAM to estimate approximate Mw. Mark Houwink equation, $[\eta] = KM^{\alpha}$ is generally used for the estimation of molecular weight of linear polymers where K and α values are constant for a particular polymer/solvent/ temperature system. For PAM the values of K and α are 6.31×10^{-5} and 0.80, respectively.

FLOCCULATION

Settling test

The test uses a 25 mL stoppered graduated cylinder and stop watch. The slurry sample is placed in the cylinder, the chemical is added, and the cylinder is inverted 10 times. After mixing, the cylinder is set upright and the height of interface between the supernatant liquid and setting solid bed is measured over time. The settling test is carried out using kaolin suspensions. The settling tests for all graft copolymers of Dx with PAM are carried out in kaolin suspension. In each case, the settling time is plotted against the height of interface.

Jar test

The flocculator is supplied by M.B. Flocculators, Bombay, India. It consisted of six pedals on a bench connected to each other by gear mechanism. All the

TABLE II
Particle Size, Chemical Composition, and Zeta Potential of Kaolin Suspensions

Sample	Particle size (nm)	Zeta potential (mV)	Fe$_2$O$_3$ (%)	SiO$_2$ (%)	Al$_2$O$_3$ (%)
Kaolin	3.8	−27.54	0.25	46.25	39.13

TABLE III
Intrinsic Viscosity and Molecular Weight Details of Graft Copolymers

Polymer	Intrinsic viscosity [η]	M_w (×10⁶)	Grafting efficiency (GE%)
Dx-g-PAM1	8.34	2.61	83.23
Dx-g-PAM2	8.50	2.67	78
Dx-g-PAM3	8.62	2.72	86.45
Dx-g-PAM4	8.02	2.48	76.51

GE% = wt. of grafted chains/wt. reacted monomers× 100.

pedals are simultaneously rotated by the same motor, with the provision for speed control. The following procedure is adopted uniformly in all the cases. In 1-liter flocculation jars, 400 mL of the flocculating suspension is taken. For the synthetic suspensions, 1 wt % solids content is chosen. The jars are placed on the flocculator bench dipping the stirrer blades in the suspension. Dilute polymer solution of 10⁻⁴ g/mL concentration is added to each jar under slow stirring condition. Immediately after addition of polymer to all the jars, the suspensions are stirred at a constant high speed of 75 rpm for 2 min followed by slow stirring at 25 rpm for 5 min. The flocs developed during slow stirring are allowed to settle down for 10 min. Clean supernatant liquid is drawn and its turbidity is measured by digital Nephelo Turbidity meter. The turbidity is expressed in Nephelo Turbidity Unit (NTU). Turbidity vs. Polymer Dosage graph was then plotted.

Calculation of settling velocity

The flocculation performance of a particular polymer can be correlated with the settling velocity. The greater the settling velocity of the floc containing contaminants, the better will be its flocculation performance. From the settling curves, it is observed that the fall of interface is linear for a considerable height before it becomes nonlinear. This means that the rate of fall of the interface is constant initially, after which it gradually declines. Initial settling rate is calculated from the slope of the linear portion of the settling curves. In this study it is observed that satisfactory linearity is maintained for about 20 cm fall of the interface height in case of kaolin suspension.

RESULTS AND DISCUSSION

Intrinsic viscosity measurements

The intrinsic viscosities of dextran and the graft copolymer are shown in Table III. With grafting of PAM chains onto the polysaccharides backbone, two extreme situations are possible. One can have either a large number of short PAM chains or a small num-

ber of long PAM chains. In the former case, the original compact shape of polysaccharide would not be changed to a greater extent because of the presence of a large number of short PAM chains. This would result in lower hydrodynamic volume. By contrast, presence of small number of longer PAM chains would change the shape of polysaccharide to a greater extent, thus increasing its larger hydrodynamic volume. This is reflected in its high intrinsic viscosity value. Thus, along a series of graft copolymers, fewer and longer PAM branches leads to higher intrinsic viscosity. Thus in case of Dx-g-PAM3, an increase in intrinsic viscosity is obtained because of the optimum CAN concentration at the constant acrylamide concentration.

### Calculation of approximate molecular weight

It has been observed that due to the longer PAM chains, Dx-g-PAM3 has highest molecular weight than the other graft copolymers. The results of Mw of graft copolymers are shown in Table III.

Flocculation studies

In kaolin suspensions, the optimum flocculant dose is found to be 10 ppm (Fig. 1). Long chain polymers when added in small dosage to a suspension of
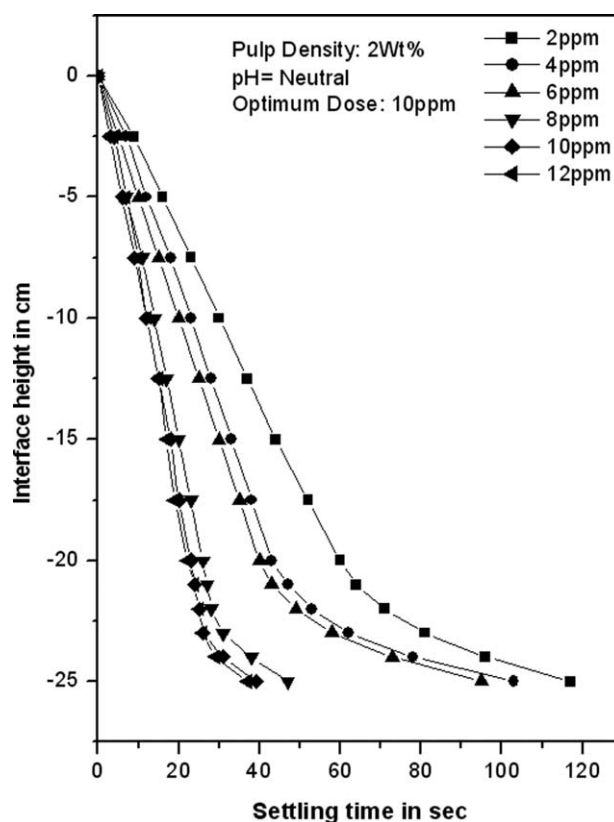
Figure 1 Settling curves for kaolin suspension using different dose of Dx-g-PAM3.
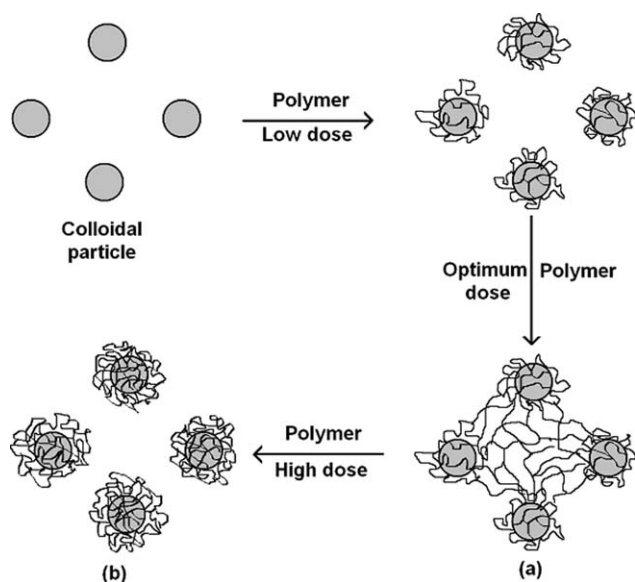
Figure 2 Schematic illustration of (a) bridging flocculation and (b) restabilization of adsorbed polymer.

colloidal particles, adsorb onto them in such a manner that an individual chain can become attached to two or more particles thus "bridging" them together (Fig. 2). However, interestingly this phenomenon is observed up to a particular optimum polymer dosage beyond which flocculation diminishes, a process being known as steric stabilization. The essential requirements for polymer bridging are that there should be sufficient unoccupied particle surface for attachment of polymer segments from chains attached to other particles and that the polymer bridges should be of such an extent that they span the distance over which interparticle repulsion prevails. Thus, at lower dosages, there is insufficient polymer to form adequate bridging links between particles. With excess polymer, there is no longer enough bare particle surfaces available for attachment of segments and the particles become restabilised, which may involve some steric repulsion. On average, bridging flocculation gives aggregates (flocs) which are much stronger than those produced by addition of salts (i.e., by reduction in electrical repulsion).

In case of settling of kaolin suspension with graft copolymer of dextran, settling time is observed. Using steady increase in polymer dose from 2 to 12 ppm, it is note that at a certain polymer dose of 10 ppm the settling time reduces to minimum. At higher dose of 12 ppm there is no significance increasing in settling time. Thus 10 ppm is the optimum polymer dose where the bridging is maximum which results to better flocculation performance.

Figure 3 compares the flocculation efficiency of Dx-g-PAM1 to Dx-g-PAM4 in kaolin suspension. It is apparent from the figure that the flocculation per-

formance of Dx-g-PAM3 having fewer but longer PAM chains (as evident from the intrinsic viscosity values), is better than that of other graft copolymers.

Figure 4 shows the comparison of the flocculation performance of Dx, PAM, and Dx-g-PAM3 in kaolin suspension. It has been observed that Dx-g-PAM3 shows better performance than PAM and Dx. The graft copolymers show better performance when compared to the base polysaccharides, because the presence of the dangling longer branches of PAM onto rigid polysaccharide backbone which leads to better approachability toward the contaminants as per Singh's Easy Approachability Model.[16] The flocculation characteristics of the graft copolymers are caused by polymer bridging.[17] For effective bridging to occur, the length of the grafted chains should be longer so as to adsorb on a particle surface to another particle surface. Hence, the polymer with longer grafted chains would be more effective than that with shorter chains, which has been observed in Dx-g-PAM3.

In Figure 5 the efficiency of Dx-g-PAM3 has been compared with those of three commercial flocculants, namely, Magnafloc LT22, Rishfloc 440 HV, and Rishfloc 226 LV in kaolin suspension. Dx-g-PAM3 has been chosen among the other graft copolymers because this is the best-performing graft
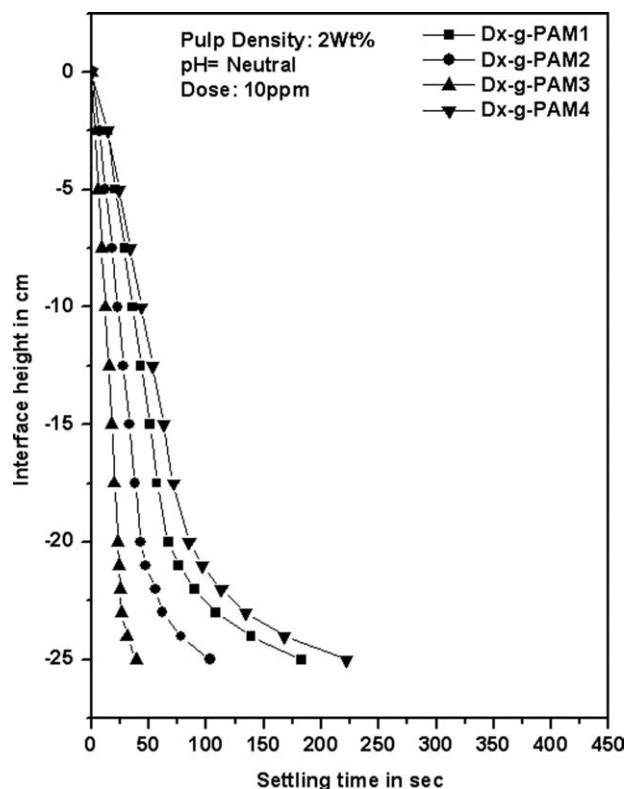
Figure 3 Settling curves for kaolin suspension using various grades of Dx graft copolymers.
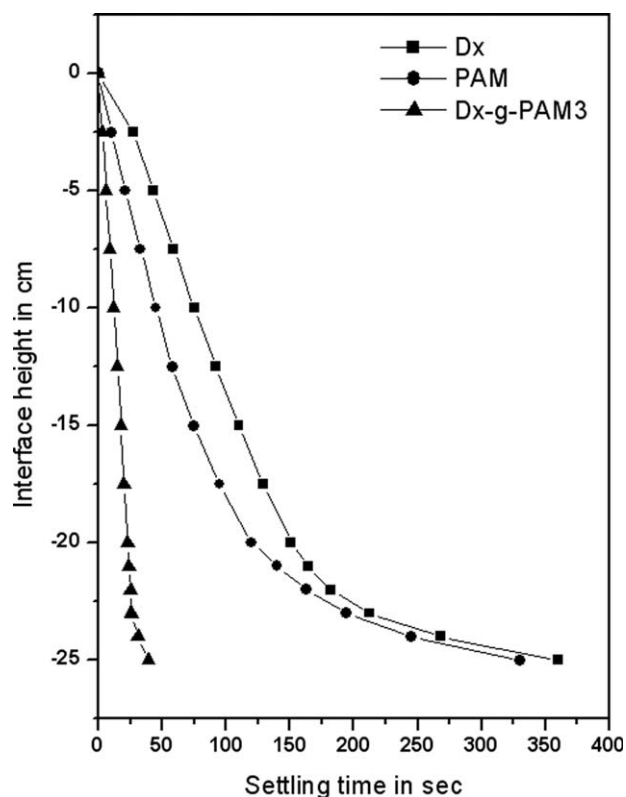
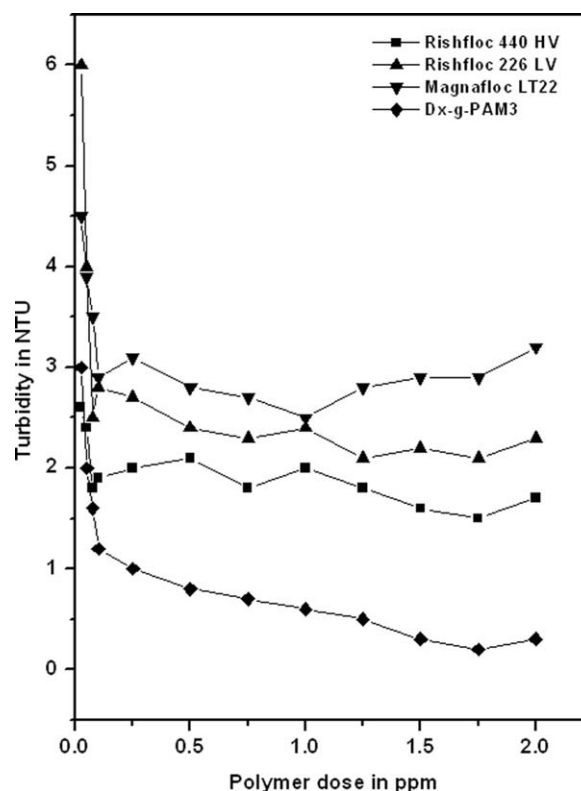**Figure 4** Settling curves for kaolin suspension using Dx, PAM, and Dx-g-PAM3.

Figure 6 Flocculation performance for kaolin suspension using Dx-g-PAM3 and commercial flocculants.
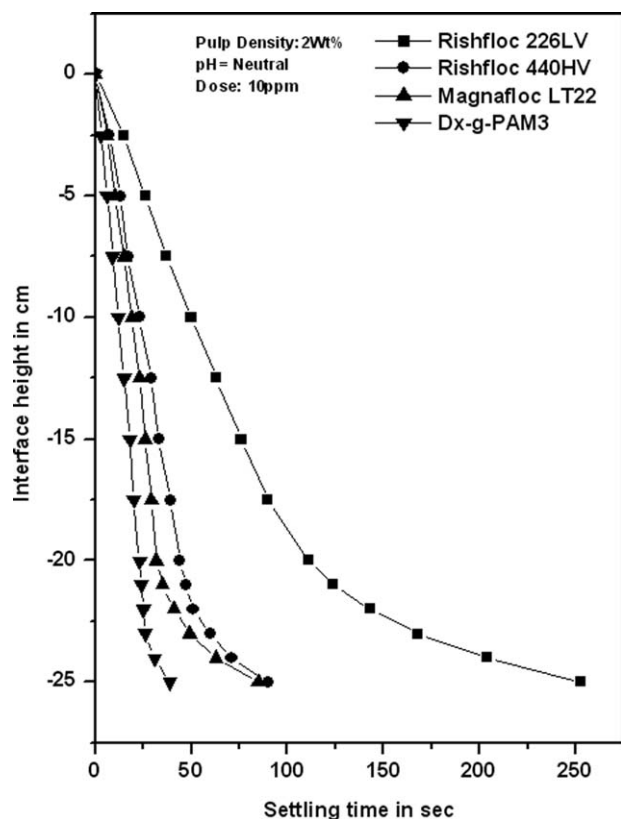
copolymer among all the graft copolymers. Here, the graft copolymer dominates the commercial flocculants in terms of flocculation efficiency. In case of linear polymers, the polymer segments attach to the surface in trains, project into the solution as tails or to form a part of loops, which link tail together. By this way, they can form bridges between the colloidal particles to form flocs. In the case of graft copolymers, due to the better approachability of the grafted chains, they can easily bind the colloidal particles through bridging. This type of intense bridging is not possible in case of linear polymers.

From jar test results, it has been observed from Figure 6 that Dx-g-PAM3 shows best performance (low turbidity) among the other commercial flocculants i.e., steepest turbidity versus polymer dose curve is obtained by its addition in the kaolin suspension.

Settling velocities

The settling velocities of the kaolin suspensions with the addition of dextran, graft copolymers, and commercial flocculants are calculated and the values are given in Table IV. Among all the graft copolymers the settling rate with addition of Dx-g-PAM3 is found to be more than the others. This is also the trend of flocculation behavior as discussed earlier.

Figure 5 Settling curves for kaolin suspension using Dx-g-PAM3 and commercial flocculants.

TABLE IV
Settling Velocities of Kaolin Suspension with Addition of Dextran, Graft Copolymers and Commercial Flocculant

Polymer	Settling velocity (cm/s)
Dx	0.1324
Dx-g-PAM1	0.299
Dx-g-PAM2	0.4651
Dx-g-PAM3	0.8695
Dx-g-PAM4	0.2352
Magnafloc LT22	0.625
Rishfloc 440HV	0.4545
Rishfloc 226LV	0.1801

CONCLUSION

From an analysis of the conducted settling test studies, it can be concluded that by grafting PAM chains onto dextran, effective flocculating agents can be developed for the treatment of waste-water. Of the grafted products, Dx-g-PAM3 shows better performance than the other grades of graft copolymers in kaolin suspensions. The performance of Dx-g-PAM3 is also better than that of other commercial flocculants. Variation in the CAN concentrations results in a series of graft copolymers having varying number and length of PAM chains which leads to different intrinsic viscosities and different molecular weights of various grades of graft copolymers. Dx-g-PAM3 can be used industrially as effective flocculant at various conditions as it out performs various commercial flocculants.

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