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High-technology materials based on modified polysaccharides*

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Abstract: Polysaccharides are abundantly available from farm, forest, and microbial resources. They are used in myriad applications. It has been established in the authors' laboratory that their performance is enhanced considerably on purification, grafting by polyacrylamide (PAM), and subsequent hydrolysis as well as cationization. The most significant performance is enhanced in flocculation where it has been found that the modified polysaccharides outperform existing flocculants in national and international markets. Similar effects are observed in their performance in turbulent drag reduction (DR), percolation, and rheology. The present article outlines the details of materials, mechanisms, and practical applications of these novel materials.

Keywords: polysaccharides; polyacrylamide grafting; modified polysaccharides; flocculants; drag reduction.

INTRODUCTION

The global production of polymeric materials is now more than 200 million tonnes per year. Plastics consume 4 % of the extracted crude oil. On the other hand, biomass production per year is approximately 50 billion tonnes. The current crisis in the price of oil, which has upset all of the world's economies, and the consequent inflationary regime is subjecting billions of people around the world to unpremeditated suffering. Thus, it is advisable to develop useful polymers from biomass. Polysaccharides can be obtained either from tree extrudates or from agricultural crops. Some useful polysaccharides can be produced by biotechnical routes.

Water-soluble polysaccharides have myriad industrial and agricultural applications as viscosity controllers [1], drag reducers [2], flocculants [3], controlled drug delivery agents [4], adsorbent polymers, responsive polymers, dispersants, stabilizers, crystal growth inhibitors, materials-soluble packaging agents, water-borne polymer coatings, and adhesives, etc.

Polysaccharides have various characteristics. They are biodegradable, shear-stable, inexpensive, and easily available from renewable farm and forest resources. Depending on the source, these poly-

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saccharides may have many low-molecular-weight impurities. The biodegradability of polysaccharides reduces their shelf life and needs to be suitably controlled. In various applications, their required dosages are large and their solutions and flocs lose stability and strength because of biodegradability. However, by purification [5], grafting [5], hydrolysis [6], and cationization [7], useful polymeric materials can be developed for varied applications.

Effluent disposal is a major problem nowadays all over the world. Industrial development has created hazards and environmental problems. Hence, environmental concern and depletion of raw material resources have forced scientists and technologists to develop materials from renewable agricultural and plant resources to protect the environment from pollution.

Recycling of domestic wastewater, industrial effluents, and mineral-processing effluents has been accepted by the application of synthetic flocculants for solid–liquid separation due to economic and environmental considerations all over the world [8–10]. When polymers are involved in a solid–liquid separation by an aggregation process of colloidal particles, the process is termed “flocculation” [10]. In general, flocculation is caused by the addition of a minute quantity of chemicals known as “flocculants”. Both inorganic and organic flocculants are used in various kinds of flocculation phenomena [11]. Among the inorganic flocculants, the salts of multivalent metals like aluminum and iron are mostly used. The organic flocculants are essentially polymeric in nature. Both synthetic and natural water-soluble polymers are used as flocculants [8–11]. Some of the most important types of synthetic polymers are polyacrylamide (PAM), poly(acrylic acid), poly(styrene sulfonic acid), poly(diallyl dimethyl ammonium chloride) (DADMAC), etc., the synthetic effluents are available in all three ionic forms—cationic, anionic, and nonionic. Among the natural polymers, starch, guar gum, alginates, and products based on chitin, glue, and gelatin are used as flocculants and retention aids. The extensive use of polymers as flocculants is due to their low dosage (1–5 ppm), inertness to pH changes, formation of large cohesive flocs, and versatile tailorability. Large tonnage use of inorganic compounds produces a lot of sludge, which is hardly a problem in the case of polymeric flocculants [12].

Among the polymeric flocculants, the synthetic polymers can be tailor-made by controlling the molecular weight, molecular weight distribution, chemical structure of polymers, and nature and ratio of functional groups on the polymeric backbone. Due to versatile tailorability, synthetic polymers are very efficient flocculants. However, they are not biodegradable and shear-resistant. Natural polymers, mainly polysaccharides, are moderately efficient, are shear-stable, biodegradable, inexpensive, and easily available from reproducible farm and forest resources [13]. The biodegradability of natural polymers reduces their shelf life and needs to be suitably controlled [13]. Their required dosages are large, and their solutions and flocs lose stability and strength because of biodegradability. It is evident that all polymers, whether natural or synthetic, have one or more disadvantages [14].

In the past, several attempts have been made to combine the best properties of both by grafting synthetic polymers onto the backbone of natural polymers after purification [15,16]. One of the advantages gained is the consequent reduced biodegradability because of a drastic change in the original regular structure of the natural polymer as well as the increased synthetic polymer content within the product. It is also observed that the grafting of shear degradable polymers onto a rigid polysaccharide backbone provides fairly shear-stable systems [17,18].

It has been observed that by grafting flexible PAM chains onto rigid polysaccharides such as carboxymethyl cellulose [19], sodium alginate [20], guar gum [21], hydroxypropyl guar gum [22], starch [23], amylopectin [23], amylose [24], xanthan gum [25], dextran [26], glycogen [27], and chitosan [28], it is possible to develop efficient, shear-stable, and controlled biodegradable flocculants for the treatment of industrial effluents and mineral processing. In these flocculants, the flexible chains of PAM are grafted onto a rigid backbone of polysaccharides. Hence, the approachability of PAM chains to metallic and nonmetallic contaminants increases significantly. Thus, they are endowed with highly efficient attributes. Among the graft copolymers, it has been found that the graft copolymers having fewer and longer chains are more effective flocculants. Among grafted polysaccharides of carboxymethyl cellulose, sodium alginate, xanthan gum, guar gum, hydroxypropyl guar gum, starch, amylose, amylopectin, dextran, chitosan, and glycogen have been found to be the most efficient flocculant [19–28]. Amongst all the polysaccharides, glycogen is supposed to have the highest molecular weight and is highly branched [29]. When it was grafted with PAM, it provided the best flocculation efficacy among all the modified polysaccharides, giving credence to Singh's easy approachability model [7,8,13,14,18,26,27,30].

The partial hydrolysis of PAM leads to the extended conformation in solution because of the intramolecular repulsion of their carboxyl groups. This extended conformation enhances bridging between the particles, increasing the degree of flocculation. At the same time, electrostatic repulsion may hinder adsorption if the flocculant contains too great a number of charged groups similar to those on solids [9]. Optimal hydrolysis is necessary to enhance the flocculation efficacy. A large number of grafted polysaccharides such as grafted sodium alginate [31], grafted guar gum [32], grafted hydroxypropyl guar gum [33], grafted amylopectin [34], and grafted glycogen have been optimally hydrolyzed. In all these cases, enhancement in flocculation efficiency has been observed.

These hydrolyzed and unhydrolyzed PAM grafted polysaccharides are anionic and nonionic, respectively, in nature and are effective flocculants for the relatively low negatively charged colloids. But for highly negatively charged colloidal particles, cationic polymers are more efficient.

Cationic polysaccharides can be prepared by the reaction of a polysaccharide with various reagents possessing positively charged groups such as amino, imino, ammonium, sulfonium, or phosphonium groups [35]. Cationized polysaccharides are effective flocculants over a wide range of pH. They are nontoxic and easily biodegradable. These are being used for sustained organic and inorganic matter in wastewater carrying negative charges. They are widely used as wet-end additives in paper making [36–38]. These are mainly used for controlling flocculation, retention, and paper strength [39]. Introducing a cationic group to the starch gives good mineral binding properties; this is required for anchoring the mineral to the fibers [40]. In these investigations, various cationic groups (amino, imino, sulfonium, phosphonium, etc.) have been loaded on a polysaccharide backbone.

It has been observed in the authors' laboratory that by inserting a cationic moiety (*N*-3-chloro-2-hydroxypropyl trimethyl ammonium chloride) onto the backbone of starch, amylose, amylopectin, guar gum, and glycogen [41–45], very efficient flocculants can be developed for the treatment of industrial effluents and municipal wastewater. All these cationic polysaccharides are efficient flocculants over a wide range of pH in suspensions containing high negatively charged colloids [46,47]. Furthermore, a model of flocculation has been developed [48] based on the quantitative relationship between the radius of gyration (R_G) of a flocculant with settling velocity of contaminants in various colloidal suspensions.

The drag-reducing agents are typically high-molecular-mass polymers. In industrial applications, they undergo mechanical degradation in turbulent flow. By grafting, a polymer on the backbone of another polymer affects the drag reduction efficacy (DRE). The grafted polymer undergoes degradation by flow turbulence more slowly and provides a high level of DRE at much lower concentrations than homopolymers do [2,18,49].

By assuming in each polymer chain the existence of two kinds of sequences, good (oriented along the flow direction or close to it, and strongly solvated) and poor (oriented approximately perpendicularly to the flow, poorly solvated), Brostow developed a statistical and mechanical model of drag reduction (DR) in 1980 [50]. Statistical mechanical calculations based on that model, showing, for instance, the effects of variation of the proportion of good/poor sequences on solution, did not change this situation [51–53]. Brownian dynamics computer simulations of flowing dilute polymer solutions [54,55] have shown that at short times and high shear rates, the polymer chains become less entangled and less intertwined, thus enlarging their pervaded volumes. The larger the volume pervaded by polymer chains, the higher is the DR. Acoustic measurements of the solvation numbers and of DRE show that indeed the solvation numbers go symbatically with that efficacy [56].

In the authors' laboratory, efficient, controlled biodegradation-resistant drag reducers and viscosifiers have been developed which can be used effectively at very low dosages. Their synthesis has been scaled up to pilot plant levels. The various scientific concepts have been developed, and suitable qualitative and quantitative models have been proposed to explain their characteristics. A detailed review of modified polysaccharides as flocculants, drag reducers, and rheological enhancers follows, henceforth.

MECHANISM OF FLOCCULATION

Charge neutralization mechanism

The stability of a suspension depends on the number, size density, and surface properties of solid particles of the dispersed phase and the density of the dispersion medium [9]. In an aqueous suspension, the particles of the dispersed phase usually have negative electrical charges. These negative charges are generated on the surface of solid particles in three ways [57]. First is the isomorphic substitution in the solid lattice. Second is the isomorphic substitution of surface groups (such as OH group in mineral oxides, carboxyl groups of latex particles, carboxyl or amino groups of proteins). The third method is the preferential adsorption of ions or ionizable species from the suspending medium. Because of this surface charge, ions of opposite charge in the solution will be attracted toward the surface. The counterions (e.g., Ca^{2+} or Mg^{2+}) are present in the surrounding water. They accumulate on the surface of the suspended particles. There will be a higher concentration of the counterions close to the surface than in the bulk of the liquid. This concentration falls off with increasing distance from the particle surface. Thus, there is a bound layer (Stern layer) of the counterions at the particle surface, and after this layer, a more diffused layer still exists. Only the bound layer moves with the particles. There is a plane of shear between the bound layers and the diffuse layers. The potential difference between the plane of shear and bulk solution is called the zeta potential. As the zeta potential increases, the coulombian repulsion between the particles becomes stronger and the suspension is more stable. The double layer composed of the Stern and diffusive layers is shown in Fig. 1. The flocculation occurs due to the destabilization of the colloid particles by the addition of some water-soluble polymers. Flocculation is usually taken to mean the process in which particles are interlinked by molecular chains with no change in zeta potential (ionic and nonionic organic flocculants). Coagulation, however, is taken to mean the electrical neutralization of the suspended particles as brought by iron and aluminum hydroxides.

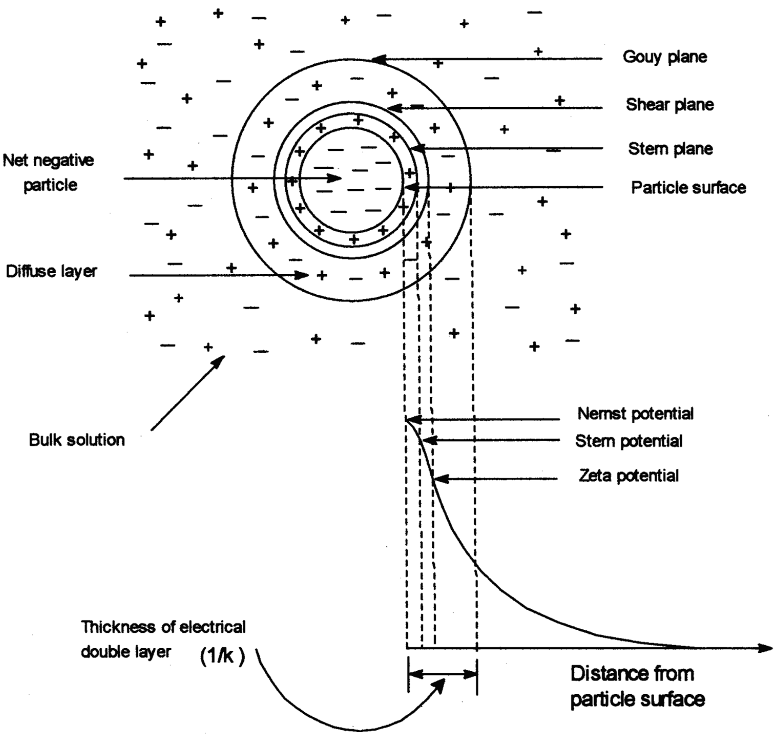


Fig. 1 Schematic diagram showing the nature of electrical forces around a colloidal particle in bulk solution.

Bridging mechanism

The major mechanism of flocculation by polymers is bridging. Ruehrwein and Ward first proposed the basic principle of bridging flocculation in 1952 [58]. They presented a model where a single polymer chain was bridging between two or more particles. The basics of this model have been subsequently refined, but the main points are unchanged, the loops and tails of the adsorbed polymer structure on one particle protrude into solution and get attached to a second particle. Smellie and La Mer [59] postulated that the surface coverage of adsorbed polymer is a fundamental parameter controlling the probability of bridging. Subsequently, Healy and La Mer [60] introduced the concept of "half surface coverage" as being the optimum condition for flocculation to occur.

When long-chain polymers [61,62] in small dosage are added to a colloidal suspension, they get adsorbed onto two or more particle surfaces and thus form a bridge [62] (Fig. 2a) between them. There should be sufficient unoccupied space on the particle surface to form polymer bridging. This phenomenon is observed up to a particular dosage of polymer beyond which flocculation diminishes, the process being known as steric stabilization (Fig. 2b). Hence, at lower dosages of polymer, there is no adequate bridging occurring between the particles. Similarly, at higher dosages of polymer, there is insufficient particle surface for attachment of the polymer segments leading to destabilization. Flocs formed by bridging mechanism are found to be larger and stronger than those produced by addition of salts. However, under high shear rates, these flocs are broken and may not reform once again. Biggs et al. [63] have studied the aggregate structures formed via a bridging flocculation mechanism. Larsson and Wall [64] have studied the flocculation of cationic amylopectin and colloidal silicic acid via bridging mechanism.

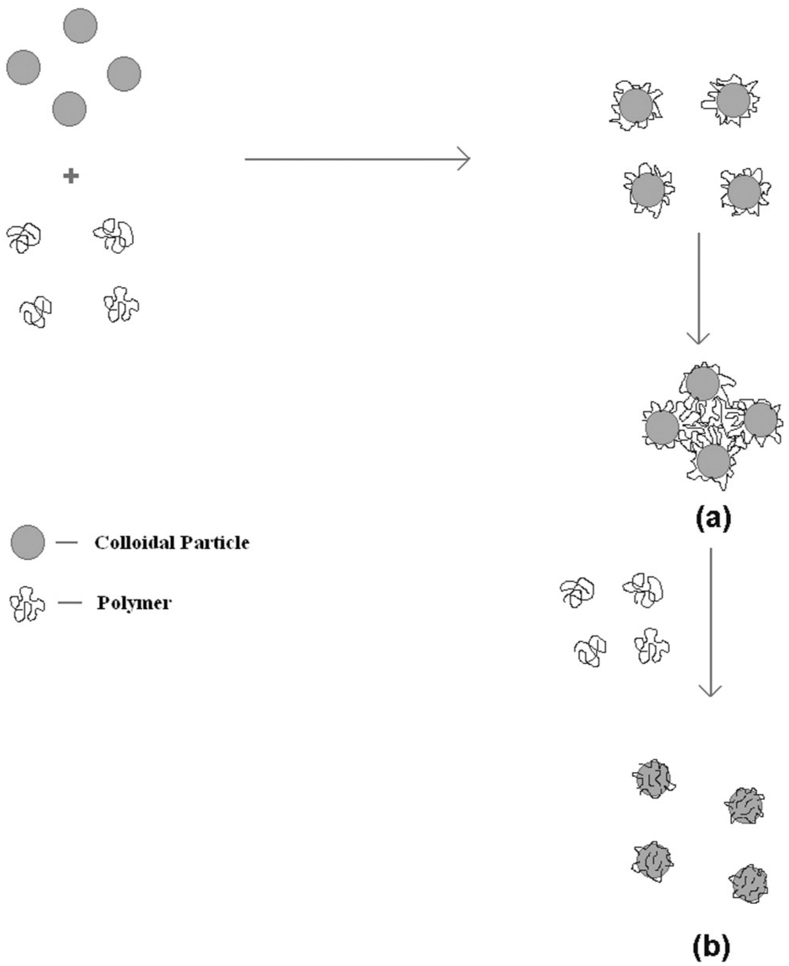


Fig. 2 Schematic illustration of (a) bridging flocculation and (b) restabilization of adsorbed polymer.

The control of the aggregate structures formed during a bridging flocculation process is not easy [65]. Parameters such as polymer chemistry, polymer charge, particle surface charge, polymer dosage, and the mixing regime are important factors. The primary factor to control is the structure of the adsorbed polymer layer, the conformation should be loops and tails types. There should also be some particles with available free surface to facilitate the bridging. In an actual flocculation process, the development of an adsorbed polymer structure occurs in a dynamic environment.

The reason for better flocculating power of the graft copolymers, hydrolyzed graft copolymers, and cationic polymers over the linear polymers is as follows: Essentially, polymer bridging occurs because segments of a polymer chain absorb on different particles, thus linking the particles together. In order for effective bridging to occur, there must be sufficient chain lengths, which extend far enough from the particle surface to attach to other particles. In the case of linear polymers, the polymer segments attach to the surface in trains, project into the solution as tails, or form parts of loops, which link trains together [66]. By this way, they can form bridges between the colloidal particles to form flocs, as shown in Fig. 3.

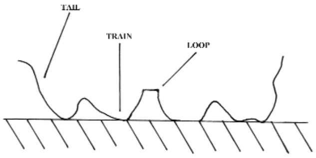
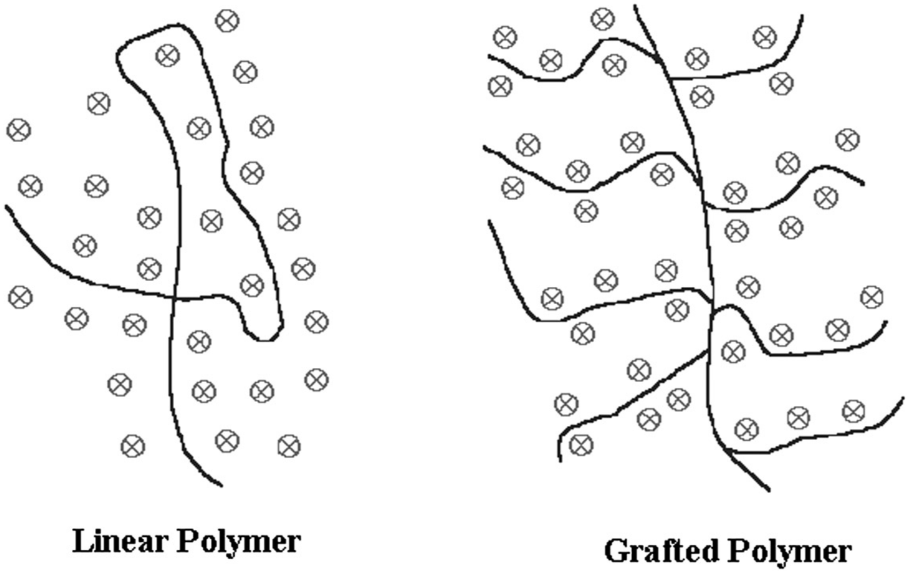


Fig. 3 Configuration of an adsorbed polymer chain [G. J. Fleer et al. (1933)].

Singh's easy approachability model

The flocculation efficiency of graft copolymer is much higher than polysaccharide and PAM. In graft copolymers, the grafted PAM branches on rigid polysaccharides form flexible comb-type structures (Fig. 4) and have higher approachability to contaminants. The approachability increases with a higher-molecular-weight branched polysaccharide backbone with flexible grafted PAM chains. Such grafted polysaccharides have a higher R_G. Among all grafted polysaccharides, PAM grafted glycogen has the highest R_G. Glycogen is a highly branched, highest-molecular-weight, water-soluble polysaccharide. Its graft copolymer provides the best performance. The easy approachability model was proposed by Singh in 1995 [18] and is discussed in detail later on [8,13,30].


Linear Polymer

Grafted Polymer

Fig. 4 Singh's easy approachability model.

Brostow, Pal, and Singh's flocculation model

This model is based on above concept that effective flocculants pervade large volumes of liquids in the suspension. Since many flocculants are polymers, a good flocculant according to this model should have higher R_G. The authors assume a connection between R_G and settling velocity (y) of particles out of suspension. Four different types of aqueous suspensions were studied (silica, coal, Mn ore, and Fe ore). A unique relationship is demonstrated between R_G and y for several polymeric flocculants in each type of suspension [48]. For each suspension type, the corresponding equation has the form

$$y = a\, R_G{}^{b}$$

where two parameters, a and b, characterize the suspended particles and the liquid medium.

EXPERIMENTAL

Materials and methods

Various polysaccharides were obtained from commercial sources. Analar grade acrylamide was obtained from E. Merck, Germany and was recrystallized from acetone prior to use. Analar grade of ceric ammonium nitrate was supplied by E-Merck (I) Pvt. Ltd., Mumbai, India. *N*-3-chloro-2-hydroxy propyl trimethyl ammonium chloride was purchased from Lancaster Synthesis Ltd., UK. Double-distilled water was used during synthesis and solution preparation.

To elucidate the flocculation efficacy, we used five types of suspensions. Silica was supplied by Jyoti Chemicals, Mumbai, India. Coal sample (R-7 Jhanjra) was a gift from Coal Mines, Jharkhand, India. Fe and Mn ores were gift samples by Joda Mines, Jharkhand, India. Kaolin was supplied by B. D. chemicals, Howrah, India. The detailed characteristics of these five suspensions are tabulated in Table 1.

Table 1 Detailed characteristics of various colloidal suspensions.

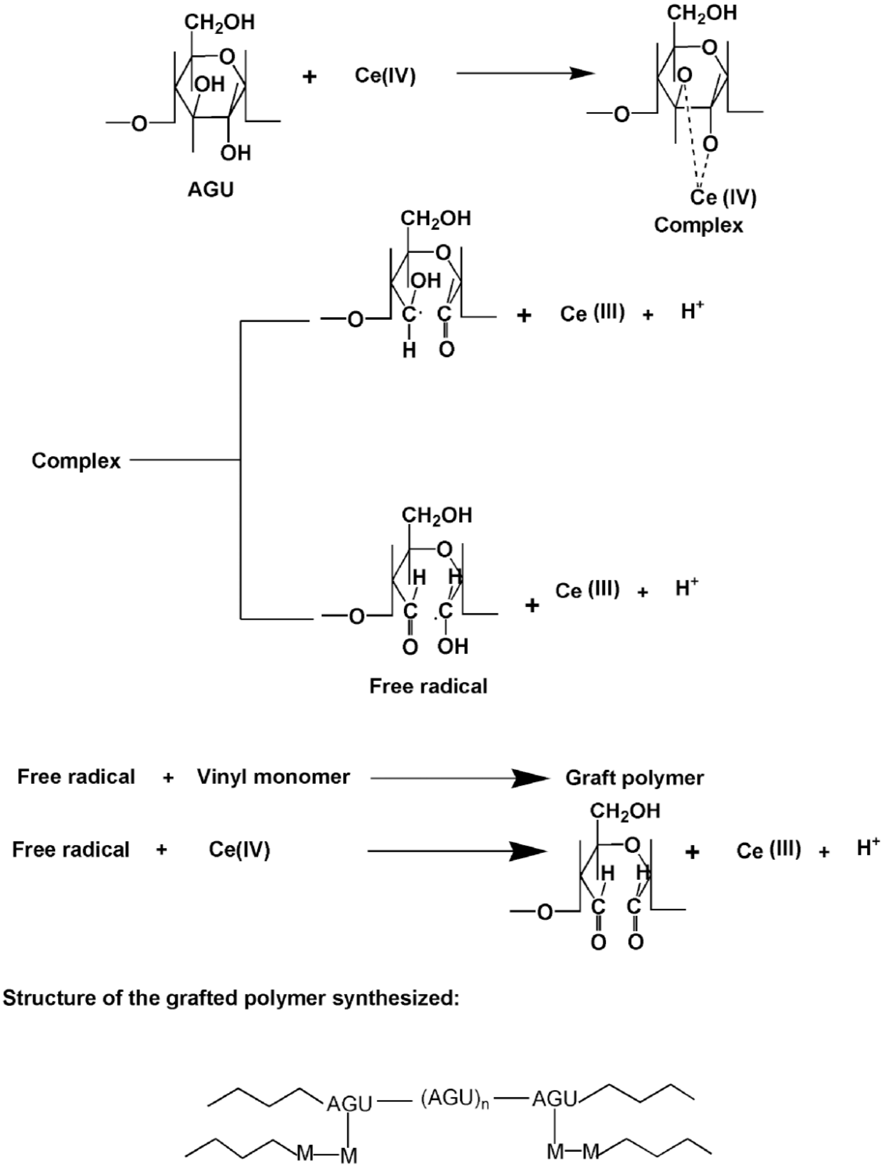
Suspension	Particle size (nm)	Sp. gravity (gm/cc)	Zeta potential (mV) at neutral pH
Silica	102.3	3.10	–53.5
Fe ore	105.7	3.45	–32.45
Kaolin	5.6	2.0	–2.40

Purification of polysaccharides

Natural polysaccharides contain proteins, fats, and fiber materials as impurities. They were subjected to Soxhlet extraction for about 70 h using 95 % ethyl alcohol as suggested by Whitcomb and Mackoskow [67].

Graft copolymerization

The various graft copolymers had been synthesized by ceric ion initiated solution polymerization technique [68,69]. In this technique, the free radicals are formed exclusively on the polysaccharide molecules, thus minimizing the homopolymers formation. Further, the acrylamide and ceric ammonium nitrate concentrations were kept below 2.0 and 0.1 M, respectively, within the limit of Owen and Shen [70] to ensure grafting and minimal homopolymer formation. The extraction of occluded PAM was carried out by solvent extraction with a mixture of formamide and acetic acid (1:1 by volume) [71]. Scheme 1 shows the graft copolymerization and purification.



Scheme 1 Synthesis and purification of graft copolymers.

Hydrolysis of graft copolymers

The best-performing grades of graft copolymers were chosen for partial hydrolysis with KOH. The hydrolysis procedure is as follows:

The required amount of graft copolymer was dissolved in distilled water. Then the required amount of 1 (M) KOH solution was added to it. This mixture was placed in a thermostatted water bath at a specified temperature. At the end of the required reaction time (1–6 h), 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. The reaction proceeds as depicted in Scheme 2.

Required amount of graft copolymer was dissolved in 200 cc distilled water.

↓

Then the required amount of NaOH was added to it.

↓

The mixture was placed in a thermostatted water bath at specified temperature.

↓

At the end of the required reaction time the content of the flask was poured into 400 ml ethyl alcohol.

↓

The product was filtered and washed with ethanol-water mixture (70:30) and finally with ethanol.

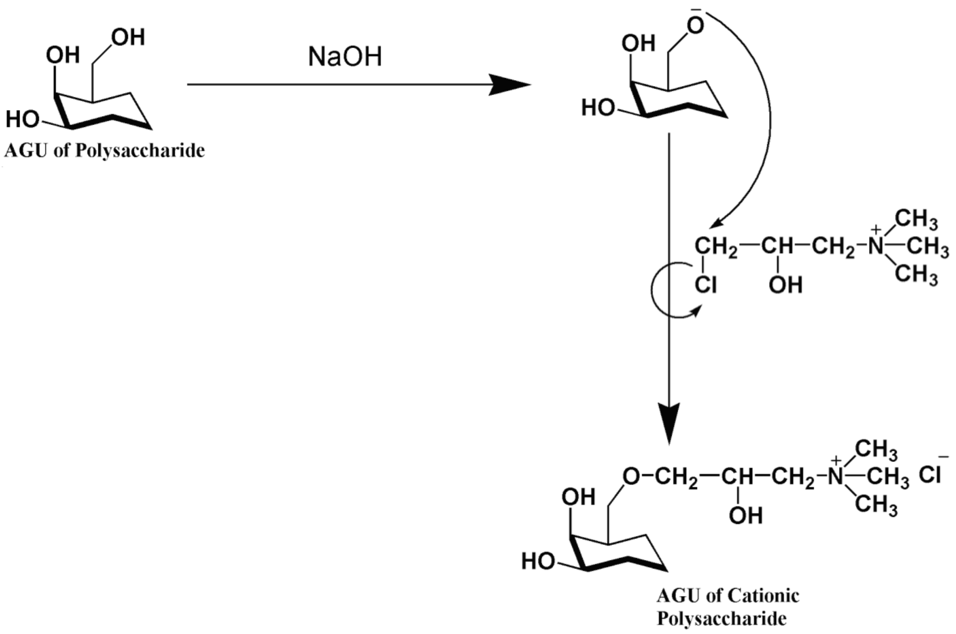
↓

It was then dried in a vacuum oven.

Scheme 2 Schematic representation for the synthesis of hydrolyzed PAM grafted polysaccharide graft copolymer.

Synthesis of cationic polysaccharides

The polysaccharides have been cationized by inserting a cationic monomer *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride onto the backbone of polysaccharide in the presence of sodium hydroxide and dilute HCl [64]. The reaction follows the mechanistic pathway as shown in Scheme 3.



AGU = Anhydroglucose unit

Scheme 3 Schematic representation for the synthesis of cationic polysaccharides.

Characterization

PAM grafted polysaccharides, hydrolyzed PAM grafted polysaccharides, and cationic polysaccharides were characterized by means of a variety of materials characterization techniques such as Fourier transform infrared (FTIR) spectroscopy, NMR spectroscopy, elemental analysis (C, H, N analysis), intrinsic viscosity measurement, thermal analysis, determination of molecular weight and R_G by SLS analysis, and morphology study by X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis. All these techniques confirm the grafting of PAM on the backbones of polysaccharides [30], hydrolysis of grafted polysaccharides [31], and insertion of cationic moiety on polysaccharides [41].

Flocculation investigations

The flocculation efficacy of these modified polysaccharides has been obtained by carrying out a jar test and a settling test.

One of the most common pieces of bench test apparatus found in water treatment laboratories to identify potential coagulation-flocculation conditions in liquid suspensions is the jar test apparatus. The test is used to confirm the preferred chemicals and also to identify the best concentrations. The flocculator used was supplied by M. B. Instruments, Mumbai, 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 colloidal suspension (prepared by dispersing 1 g of it in 400 cc of distilled water) was used for the flocculation study. The suspension was taken in each of four 1-L beakers, and the flocculant was added in solution form. The flocculant dose was varied from 0.025 to 1 ppm. The following procedure was uniformly applied for all the flocculants. Immediately after addition of the flocculants, the suspension were stirred at an uniform speed of 75 rpm for 2 min followed by a slow stirring at 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 turbidity meter. The lower the turbidity, the better will be the flocculant.

The settling test employs a 100-mL stoppered graduated cylinder and stopwatch. First of all, the suspension sample is taken in the cylinder and then polymer solution is added to it. The cylinder is inverted 10 times for thorough mixing. After that, the cylinder is set upright and the height of interface between water and settling solid bed is measured over time.

Drag reduction characteristics

A pressurized capillary flow system was used for DR measurements. The friction factor was evaluated from pressure drop and volume of flow measurements at different Reynolds number.

Rheological investigations

The rheological investigations were conducted using Controlled-Stress TA Instruments AR-1000 Advanced Rheometer. The temperature of the system was maintained at 30 °C throughout the experiments.

RESULTS AND DISCUSSIONS

Synthesis and flocculation efficacies

Hydrolyzed and unhydrolyzed PAM grafted polysaccharides and their application as flocculants

In the authors' laboratory, several graft copolymers have been synthesized by grafting flexible PAM onto the rigid polysaccharide backbones. It has been observed that amongst various graft copolymers developed in the authors' laboratory, grafted glycogen gave the best performance in flocculation [27] (Fig. 5). This is because glycogen has a highly branched structure and a very high molecular weight, and thus the approachability of the contaminants toward the branched polysaccharides enhances the flocculation efficacy, which testifies to Singh's easy approachability model.

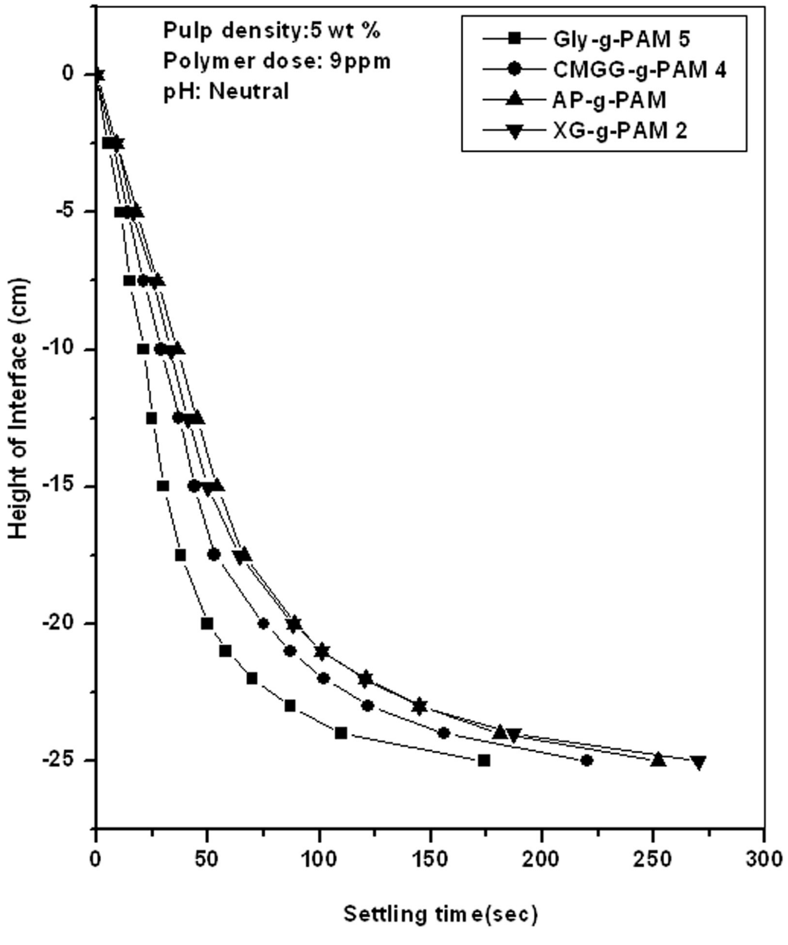


Fig. 5 Settling characteristics of kaolin suspension with various grafted polysaccharides.

Optimized grafted glycogen that performs the best as flocculant on a laboratory scale was thereafter compared with some of the commercial flocculants available in national and international markets, and it was found that our laboratory-synthesized polymer surpasses most of the commercial flocculants (Fig. 6) in performance.

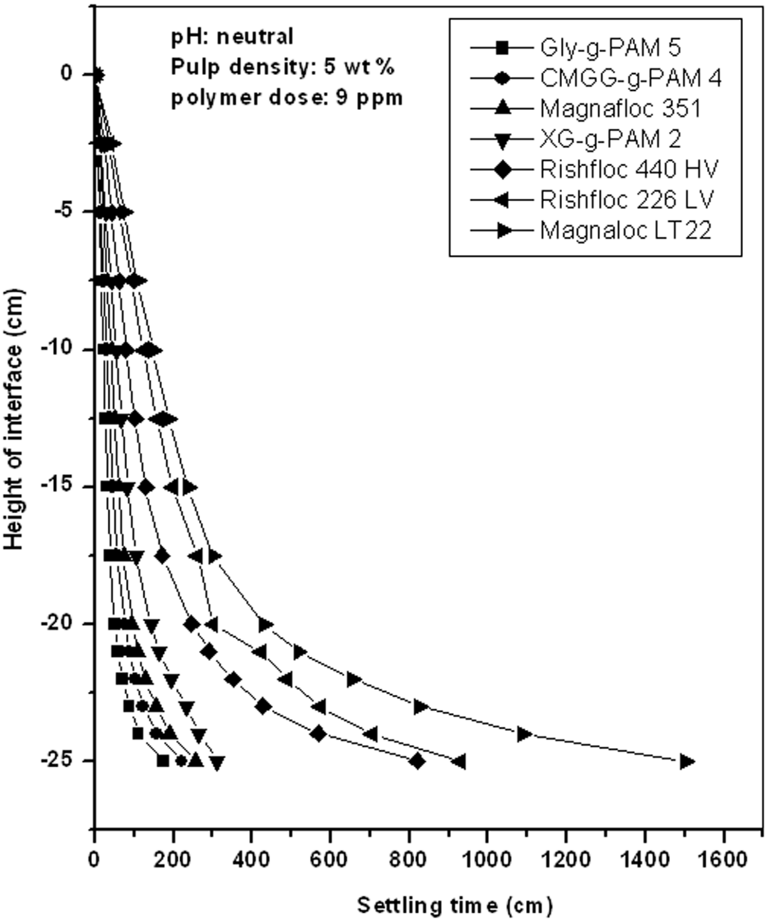


Fig. 6 Settling characteristics of kaolin suspension with grafted and commercial flocculants.

The best performing graft copolymer was further hydrolyzed in the presence of sodium hydroxide. It has been observed that the optimized grade of hydrolyzed graft copolymer surpasses the flocculation efficacy of graft copolymer in a low negatively charged colloidal suspension (Fig. 7). This is because after hydrolysis of the grafted polysaccharide, the flocculant becomes anionic and gets further extended due to coulombian repulsion, increasing its efficiency.

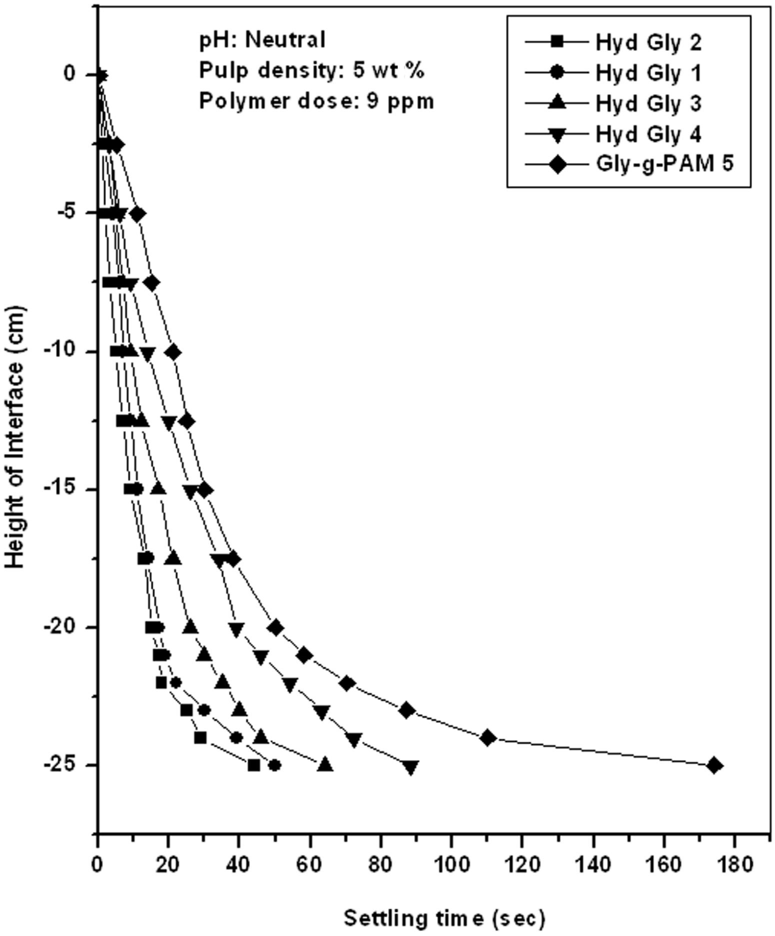


Fig. 7 Settling characteristics of kaolin suspension with addition of Gly-g-PAM 5 and various grades of hydrolyzed grafted glycogen.

Cationic polysaccharides and their application as flocculants

Although a number of methods are available for incorporating a cationic moiety onto the backbone of polysaccharides, *N*-(3-chloro-2-hydroxypropyl) trimethyl ammonium chloride has been preferred as a cationic moiety over recent years [72,73]. This is because polysaccharides are an effective backbone polymer for inserting a cationic moiety using a quaternary ammonium compound.

For each polysaccharide (i.e., amylopectin, amylose, starch, glycogen, guar gum), various grades were developed to optimize their flocculation efficacy. It has been found that the one with the longer CHPTAC chain on the backbone of the polysaccharide is the best flocculant [42–48]. When the flocculation characteristics of the best-performing cationic polysaccharides were compared to each other in silica suspension (silica suspension has a very high negative zeta potential value, –53.5 mV at neutral pH), it has been found that cationic glycogen shows the best flocculation efficacy compared to others (Fig. 8). This is because of the high molecular weight and highly branched nature of glycogen. This enhancement in flocculation efficacy conforms with Singh's easy approachability model [7,8,13,14,18,26,27,30].

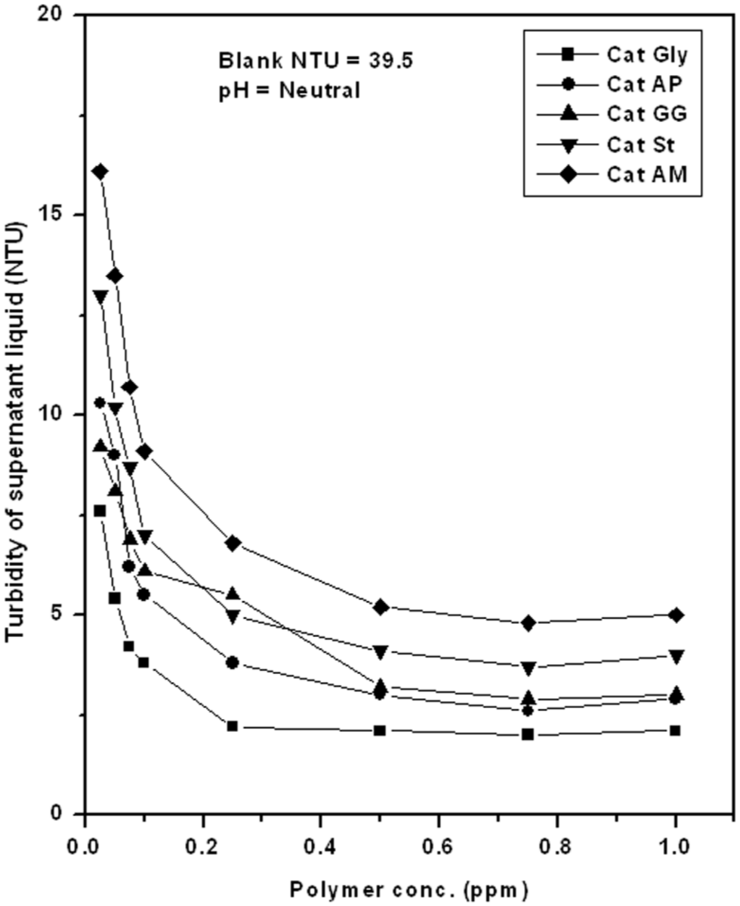


Fig. 8 Jar test results in 0.25 wt % silica suspension using Cat AP3, Cat AM, Cat Gly4, Cat GG4, and Cat St3 as flocculants. [S. Pal et al. *Colloids Surf., A* (2006)].

Further, an attempt had been made to compare the flocculation efficacy of the best-performing cationic polysaccharide (i.e., cationic glycogen) with some of the commercial flocculants (Fig. 9), namely, Magnafloc LT 22 (Mag LT 22, cationic in nature), Magnafloc 351 (Mag 351, cationic in nature), Magnafloc 156 (Mag 156, anionic in nature), Rishfloc 226 LV (Rish 226 LV, nonionic in nature), and Rishfloc 440 HV (Rish 440 HV, anionic in nature) available in national and international markets. From Fig. 9, it is apparent that Cat Gly is found to be the best flocculant in Fe ore suspensions.

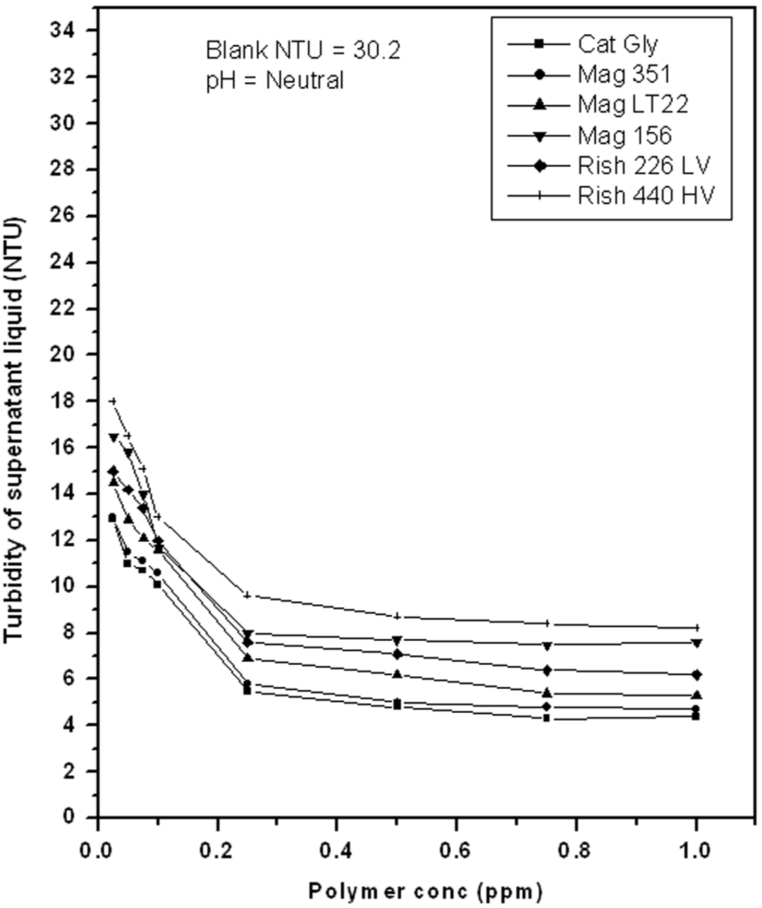


Fig. 9 Jar test results in 0.25 wt % iron ore suspension using Cat Gly4 and commercial flocculants. [S. Pal et al. *Colloids Surf., A* (2006)].

Drag reduction characteristics

Turbulent DR is the phenomenon of drastic reduction of drag by a factor of two or more below that for solvent by addition of a small amount of some substances, mainly, high polymer, fibers, soaps, surfactants, and their mixtures. Even at a concentration of a few parts per million by weight, these materials reduce turbulent intensity in flow and therefore allow liquids to flow at lesser resistance [2,18,74].

The soluble polymers are the most potential drag-reducing agents of all the additives mainly because DR up to 80 % can be obtained with the addition of a few tens of ppm by weight in a particular solvent. The polymer solution DR has been investigated in aqueous and hydrocarbon liquids. Synthetic polymers of high molecular weight ($>10^5$) are very effective drag reducers but get degraded in turbulent flows and lose their effectiveness after a short interval of time or flow. Recently, three approaches have been put forward to enhance the DRE and shear stability of polymers:

a. The DRE of polysaccharides can be enhanced by grafting synthetic PAM branches onto their main chains, resulting graft copolymers combine the efficiency of the synthetic polymer and the robustness of the polysaccharides main chain (Fig. 10).

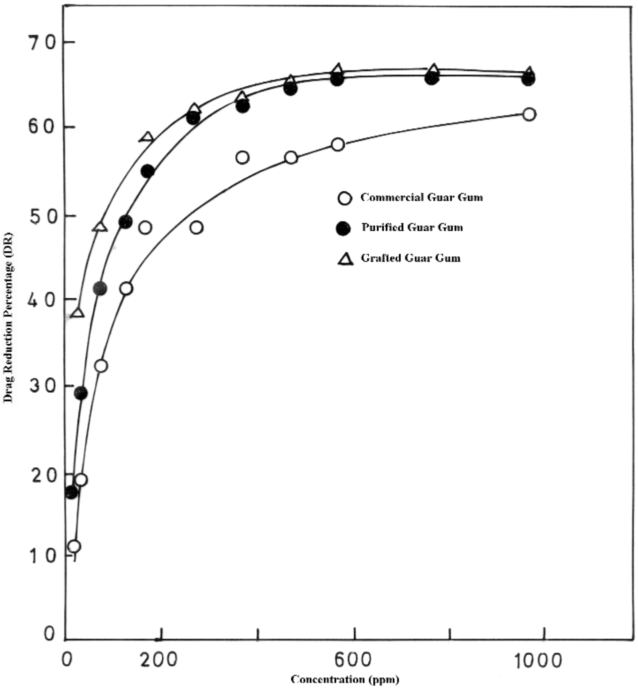


Fig. 10 DR characteristics of commercial guar gum, purified guar gum, and grafted guar gum.

b. The reversible intermolecular associations in solution increase the molecular weight of the polymer and provide mechanical stability.
c. The drag-reducing polymers (DRPs) can be cross-linked with concentrations below those required for gel formation. The presence of intermolecular cross-links leads to increased dimensions of the macromolecules, resulting in enhanced DR, although the flow-induced degradation of the polymers is not appreciably affected by the addition of cross-linking agents.

The first and third approaches have been pursued for water-soluble systems. It has been observed in the first approach that the level of DRE is higher than at low concentrations (<100 ppm) of graft copolymers and that the cross-linking is not effective in shear degradation. The characteristics of drag-reducing graft copolymers are as follows:

- Graft copolymers have high DRE and shear stability at conc. ≤100 ppm.
- DR performance of graft copolymers depends on that number and length of grafted chains.
- The solutions of graft copolymers in water are biodegradable-resistant.
- The DR characteristics of graft copolymer give credence to Brostow's polymer flow model. In 1980, Brostow [50] developed a statistical and mechanical model for DR, assuming that in each polymer chain the existence of two kinds of sequences, good (oriented along the flow direction or close to it and strongly solvated) and poor (oriented approximately perpendicular to the flow, poorly solvated). The model explained the entire phenomenon observed but it was a hypothesis without experimental evidence. This model has led to a relationship between DR, λ, and time "t" (the MDF effect), which has been confirmed experimentally for several polymer and liquid pairs [53]. Statistical and mechanical calculations based on that model showing, for instance, the effects of variation of the proportion of good/poor sequences on solution properties did not change this situation. Indirect support for the model was provided by Springer and coworkers [75] who reported the existence of a long range in homogeneities within polymer solutions. Brownian dy-

namics computer simulations of flowing dilute polymer solutions have shown that at short times and high shear rates, the polymer chains become less entangled and less intertwisted, thus enlarging their pervaded volumes. This agrees with the DR model and with the experimental results of Kulicke and coworkers [76] that the single chain can also cause DR. The practical applications of the DR phenomenon involve sometimes the concentrations as low as 10 ppm. In 1999, Brostow, Singh, and Majumdar [56] provided direct experimental evidence for the Brostow model [48]. The model assumes that the larger the volume pervaded by polymer chains, the higher is the DR. Ultrasonic measurements of the solvation numbers and of DR efficiency show that indeed the solvation numbers go symbatically with that efficacy. Recently, Brostow, Haley, Reddy, Singh, and White [49] have shown that grafted polymer undergoes degradation by flow turbulence more slowly and also provides high levels of DRE at much lower concentrations than homopolymers do.

Applications of drag-reducing polymers in agriculture

The phenomenon of turbulent DR by addition of polymers at the ppm level in fluid flow involves DR up to 80 %. Ever since the discovery of the phenomenon in World War II, efforts have been made to utilize this phenomenon for the increment of liquid flow through pipes at reduced energy input. One of the applications has been in increasing the area of coverage and reducing the energy requirement of sprinkler irrigation systems as flows in these systems (distribution pipes, risers, and injectors) are in a turbulent region.

The DRPs reduce the drag in turbulent flow yet increase the drag in a laminar flow. Therefore, using drag-reducing agents minimizes the power requirement by pumps and increases the throughput and area of coverage of sprinkler irrigation systems. Once the sprinkled water begins its laminar flow through soil, the polymers increase the drag, making water percolate slowly through the soil. In other words, water remains in the soil for a longer time, continuing to irrigate the plants instead of quickly being lost.

The major loss of water in the soil in lateritic belt is due to percolation. Hence, a reduction in percolation would be very beneficial for agriculture especially in states/countries that suffer from shortage of water.

A large number of PAM grafted polysaccharides as drag reducers have been developed in the authors' laboratory [77,78]. These grafted polymers are biodegradable and shear-stable. Of these, PAM grafted amylopectin (AP-g-PAM) has been found to reduce the percolation loss most effectively by 50 % at a concentration of 100 ppm.

Not only substantial reduction in power consumption, usage of these polymers increases the area of coverage, uniformity of water distribution, suppression of evaporation, increase in soil moisture, and soil retention and aggregation, which gives a rise in crop yield both for general crops and vegetable crops.

In another important agricultural application, the authors' group has blended the polymer with fertilizers to create slow-release fertilizers that can further reduce the cost of agriculture. This technology can be applied to insecticides. Using a slow-release urea, developed by blending urea with a tiny amount of guar gum, has boosted yields of wheat and rice by 20–25 % in field trials. A similar increase in crop yield of clustered beans, cauliflower, and brinjal has been reported. There are residual efforts with increase in crops up to 10 % in the next crop after the first application.

The cost–benefit analysis shows that using DRP in sprinkler irrigation allows a reduction in pipe diameter and power of centrifugal pump, which reduces the installation costs as well as the energy requirement. Reducing the percolation losses brings down the amount of irrigation water needed.

The above technology is applicable in micro sprinkler/drip irrigation and fertigation. If used in combination with plasticulture, it can usher in a phenomenal boost in the productivity of horticultural produce.

Rheology of polysaccharides, grafted polysaccharides, and hydrolyzed grafted polysaccharides

The shear viscosities of aqueous solutions of grafted, ungrafted, and hydrolyzed grafted polysaccharides have been measured. It has been found that:

The shear viscosities of pure polysaccharide solutions are larger over an extended range of shear rate. Since in purified polysaccharides, the low-molecular-weight impurities are extracted out, hence only high-molecular-weight contents provide higher shear viscosity. The shear viscosity increases in grafted polysaccharide solutions.

On hydrolysis, the viscosifying characteristics are tremendously increased in the cases of most of the grafted polysaccharides due to extension of partially hydrolyzed grafted PAM chains (Fig. 11). Their solutions have not only high shear viscosities but also high extensional viscosities.

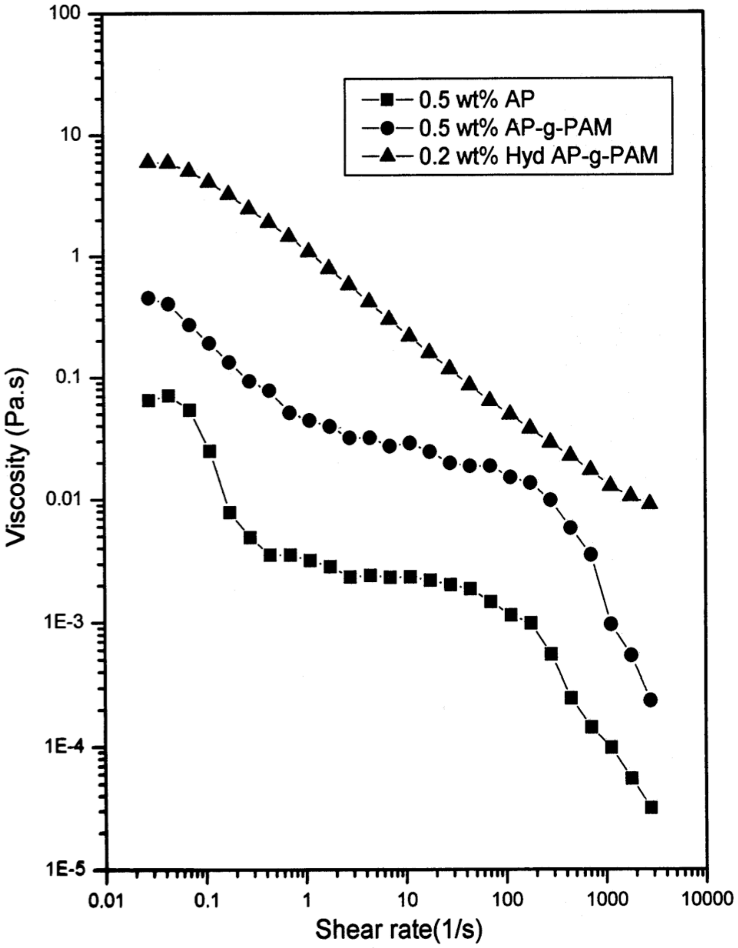


Fig. 11 Viscosity vs. shear rate curves of AP, AP-g-PAM, and hydrolyzed AP-g-PAM.

An elongational rheometer has been used to measure the extensional relaxation time λ and steady-state terminal elongational viscosities $\eta_{E,t}$ of aqueous solutions of hydrolyzed PAM grafted polysaccharides (Table 2). It has been observed by the authors [79,80] that there exist two different linear relationships for flexible and rigid polymers when steady terminal extensional viscosity vs. extensional relaxation time is plotted (Fig. 12). For semiflexible polymers, the elongational flow results in data that are intermediate to the above-mentioned limiting curves. The transitions are polysaccharides (rigid), grafted polysaccharides (flexible), and hydrolyzed grafted polysaccharides (rigid) and can be monitored by this technique. Hence, a new method that has evolved to measure the rigidity and flexibility of macromolecules at the molecular level having applications in biomedical field.

Table 2 Extensional relaxation time and extensional viscosities of aqueous solutions of hydrolyzed (hyd.) PAM grafted polysaccharides.

Polymer	Extensional relaxation time (mS)	Extensional viscosity (PaS)	Theoretical extensional viscosity	
			Rigid	Flexible
Hyd. AP-g-PAM	4.5	14.3	5.8	13.8
Hyd. CMC-g-PAM	17	11.6	21.9	52.3
Hyd. GG-g-PAM	96	105.0	123.6	295.2
Hyd. HPG-g-PAM	5.5	2.4	7.08	16.9
Hyd. SAG-g-PAM	8.7	1.34	11.20	26.8
Hyd. GG-g-PAM (500 ppm)	93.9	92.2	120.9	288.7
Hyd. GG-g-PAM (250 ppm)	8.4	11.0	10.82	25.8
Hyd. GG-g-PAM (125 ppm)	10.6	14.9	13.65	32.6

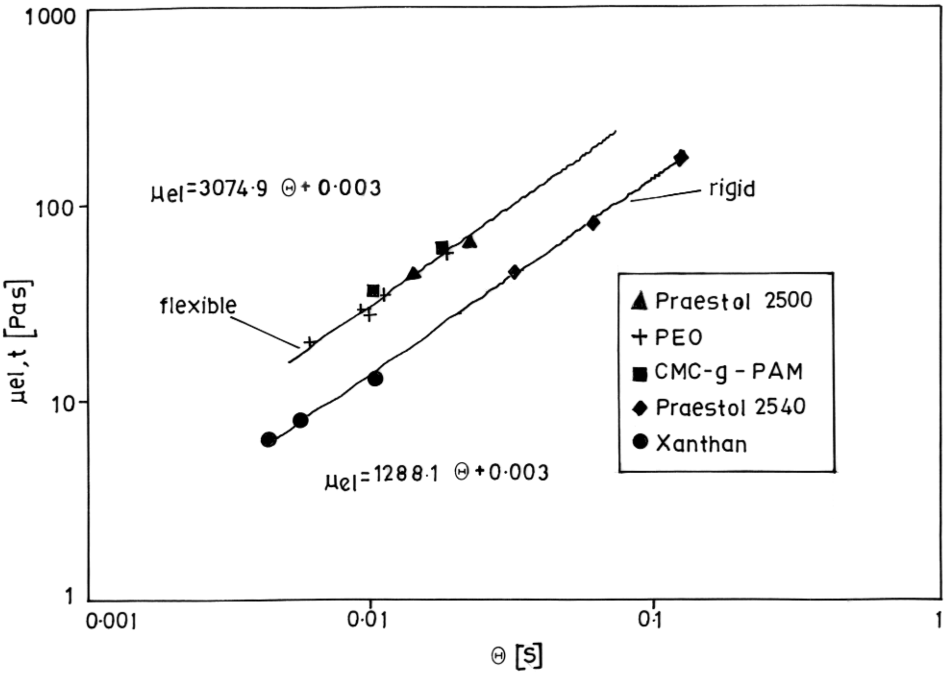


Fig. 12 Polymer flexibility/rigidity behavior of modified and unmodified polysaccharides [79].

CONCLUSION

From the above investigations, it is apparent that from inexpensive, abundant, and source-based varying-molecular-weight polysaccharides, by purification, grafting, hydrolysis, and cationization, highly efficient, shear-stable, and controlled biodegradable flocculants, drag reducers, and viscosifiers can be developed, which have myriad applications.

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