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A High Performance Flocculating Agent and Viscosifiers Based On Cationic Guar Gum

R. P. Singh,[*1] *Sagar Pal,*[2] *D. Mal*[3]

Summary: The anionic, cationic and nonionic polymeric flocculants endowed with several distinguished characteristics are being increasingly applied for the treatment of industrial effluents, municipal and wastewater. For the treatment of highly negatively charged particle suspensions, cationic flocculants are more efficient. A new route to guar gum derivatives bearing cationic groups has been developed. A series of cationic guar gums (Cat GG) have been developed by incorporating a cationic moiety *N*- (3- Chloro-2- hydroxypropyl) trimethyl ammonium chloride (CHPTAC) onto the backbone of guar gum in presence of NaOH. The various grades of cationic guar gum have been characterized by elemental analysis, FTIR spectroscopy and intrinsic viscosity measurement. The flocculation characteristics of these cationic guar gums have been evaluated in silica suspension by jar test. It has been found that among the various grades of cationic guar gums, the one with longer CHPTAC chains shows better performance. The flocculation characteristics of this best performing cationic guar are compared with those of various commercially available flocculants in silica suspension. Their rheological investigations have also been undertaken.

Keywords: cationic; flocculation; graft copolymers; guar gum; polyacrylamide

Introduction

Over recent years, considerable attention has been focused upon the treatment and disposal of wastewater sludges [1]. Flocculation has played an important role in domestic and wastewater treatment, sludge dewatering and mineral beneficiation [2–4] etc. Flocculation [5, 6] is a process of bringing together smaller particles to form larger particles, often highly porous in nature. The extensive use of polymers as flocculants is due to their distinct characteristic attributes.

In the authors' laboratory many graft copolymers have been synthesized by grafting polyacrylamide branches onto amylopectin [7], carboxymethylcellulose [8], guar gum [9] and starch [8], etc. It was postulated by one of the authors' (R. P. Singh) [10–12] that graft copolymers are more effective flocculants when compared with the linear polymers, because of the greater approachability of the dangling flexible polyacrylamide chains to the contaminant particles in their suspension. Later on, it has been found in our laboratory that amylopectin- g-polyacrylamide (AP-g-PAM) exhibits better flocculation properties in comparison with St-g-PAM and AM-g-PAM, which is due to the high molecular weight and highly branched nature of amylopectin [13, 14]. These polyacrylamide-grafted polysaccharides are nonionic in nature and are effective flocculants in the industrial effluents containing relatively low negativity contaminant particles. But for highly negatively charged colloidal particles, cationic polymers are more efficient [15].

Cationic high polymers are used as flocculating agents to remove finely divided

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[1] University of Lucknow, Lucknow – 226 007, India
Tel: + 91-522-2740467; Fax: +91-522-2740467
E-mail: vc@lkouniv.ac.in.

[2] Hindustan Gum & Chemicals Ltd., Bhiwani – 127 021, Haryana, India

[3] Department of Chemistry, IIT Kharagpur, Kharagpur – 721 302, India

solids from aqueous suspension [16]. Highly charged cationic polymers such as polyquats, polyimines and polyamines are costly. Further cationic polymers are being used for sustained organic and inorganic matter in wastewater carrying high negative charges. They are widely used as wet-end additives in paper industry [17–19].

Among various water-soluble polysaccharides, guar gum is one of the most important polysaccharide, which is having a wide variety of applications. Guar gum is the endosperm polysaccharide of the seed of *cyamopsis tetragonoloba*, which belongs to the *Luguminosoe* family [20]. It is a galactomannan consisting of backbone of α-1,4-D mannopyranosyl units, with every second unit bearing a β-1,6-D galactopyranosyl unit [21, 22]. It is easily available and cheap. India is the largest exporter of guar gum in world.

The cationic moieties have been loaded on natural polysaccharides in recent years. However no attempt has been made to develop a optimized cationic flocculant based on guar gum as native polysaccharide, their partial characterization, flocculation and rheological characteristics, which has been addressed in the present investigation.

Experimental

Materials

Materials for synthesis

Guar gum was a gift sample from Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana. *N* - (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) was obtained from Lancaster Synthesis Company, England. Analytical grade sodium hydroxide, isopropanol and hydrochloric acid were purchased from E. Merck (India) Limited, Bombay, India.

Materials for flocculation

Silica was purchased from Jyoti Chemicals, Bombay, India. The suspension zeta potential of silica is −53.5 mV.

Flocculants

Five commercial flocculants, 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) are used for comparison.

Synthesis

Guar gum has been cationised by incorporating a cationic monomer *N*- (3-chloro-2-hydroxypropyl)-trimethyl ammonium chloride onto the backbone of the polysaccharide. The details of the synthesis and the reaction conditions are as follows.

1 g guar gum was dissolved in 100 ml distilled water at room temperature. A mixture of *N*- (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride and 15 ml 1(N) sodium hydroxide was added to the guar gum solution. The reaction was then continued for 18 hours at 40–50 °C. Afterwards, dilute hydrochloric acid was added for lowering the pH below 7 to stop the cationization process [23]. The solution was thereafter cooled to room temperature and the polymer was precipitated by adding excess isopropanol. It was then dried in a vacuum oven at 40 °C for 6 hours. The details of synthetic parameters such as mole ratio of the reactants, reaction temperature and time are given in Table 1.

Characterization

Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer (CS/S: 0.003899) at 25 °C. The viscosities were measured in dilute aqueous solution. The pH of the aqueous solution is neutral. The intrinsic viscosities were evaluated as described earlier [24], which is a standard procedure for measurement of intrinsic viscosity by Ubbelodhe viscometer.

Elemental analysis

Elemental analysis of guar gum, various grades of cationic guar gums and CHPTAC was undertaken with a Carlo Erba 1108

Table 1.
Synthetic details of cationic guar gum.

Polymer	Amount of AGU ^{a} (mol)	Amount of CHPTAC (mol)	Volume of NaOH (mol)	Temp. (°C)	Time (hrs)	Intrinsic viscosity (dL/g)
Cat GG1	0.0061	0.0026	0.015	40–50	18	12.8
Cat GG2	0.0061	0.0039	0.015	40–50	18	14.0
Cat GG3	0.0061	0.0053	0.015	40–50	18	14.7
Cat GG4	**0.0061**	**0.0066**	**0.015**	**40–50**	**18**	**15.6**
Cat GG5	0.0061	0.0079	0.015	40–50	18	15.2
GG	-	-	-	-	-	8.2

elemental analyzer. The estimation of only three elements (carbon, hydrogen and nitrogen) was undertaken. The results are shown in Table 2.

FTIR Spectroscopy

A Thermo Nicolet FTIR Spectrophotometer (Model – Nexus 870 FTIR) was used and the potassium bromide (KBr) pellet method was used for FTIR study. The FTIR spectra of guar gum, cationic guar gum 4 and *N*- (3-chloro-2- hydroxypropyl) trimethyl ammonium chloride are shown in Figure 2.a-2.c respectively. Cationic guar gum 4 is the optimized grade, which has been confirmed from intrinsic

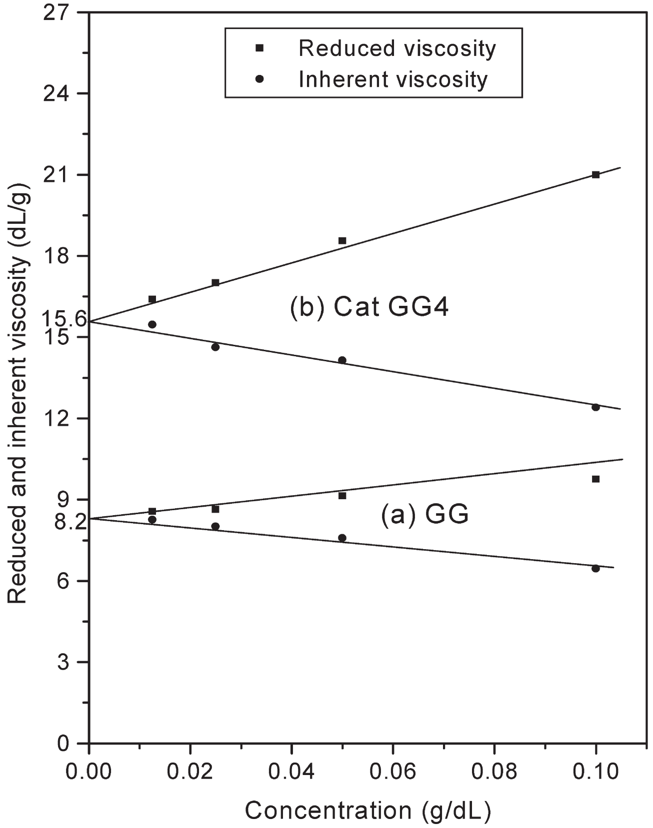

Figure 1.
Reduced and inherent viscosity vs. concentration curve for the measurement of intrinsic viscosity of (a) guar gum and (b) cationic guar gum4.

Table 2.
Elemental analysis of cationic guar gum.

Polymer	% of Carbon	% of Hydrogen	% of Nitrogen
GG	39.1	6.40	0.16
CHPTAC	37.71	7.82	7.34
Cat GG1	38.85	6.64	3.01
Cat GG2	39.25	6.20	3.22
Cat GG3	39.42	6.01	3.47
Cat GG4	**38.66**	**6.48**	**3.88**
Cat GG5	38.30	6.54	3.60

viscosity and from flocculation characteristics (Fig. 3).

Flocculation Characteristics

Flocculation tests of silica suspension were carried out by using a standard flocculation jar apparatus. The standard flocculation jar apparatus was supplied by M. B. Instruments, Mumbai, India. The turbidity measurement was carried out by the Digital Nephelo Turbidity Meter 132, procured from Systronics (Ahmedabad, India). 0.25 wt% suspension of silica (prepared by mixing 1 gm in 400 c.c. of distilled water) was used for flocculation study. The suspension was taken in each of four 1-L beakers and the flocculants were added in solution. The following procedure was uniformly applied to the suspension. Immediately after addition of the flocculant, the suspension was stirred at a constant speed of 75 rpm for 2 minutes, followed by 25 rpm for 5 minutes. The flocs were then allowed to settle down for 10 minutes. At the end of the settling period, the turbidity of the supernatant liquid was measured. The dose

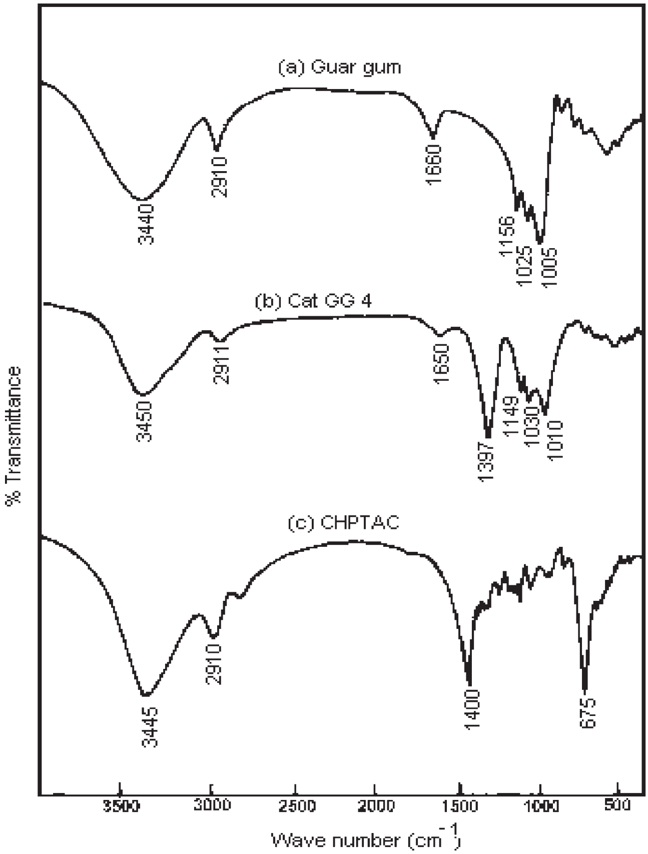

Figure 2.
FTIR spectrum of (a) guar gum, (b) cationic guar gum 4 and (c) *N* – (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride.

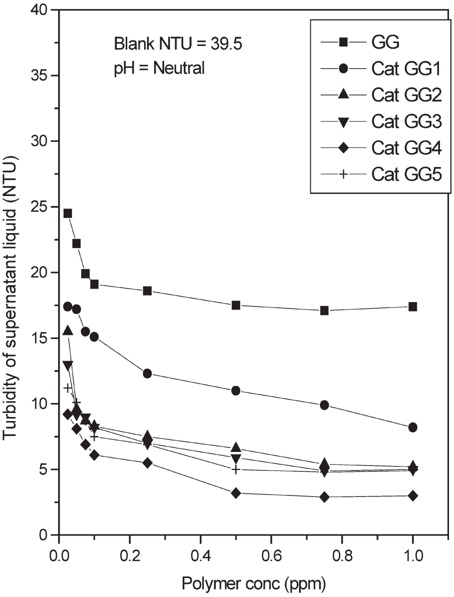

Figure 3.
Jar test results in silica suspension using Guar gum and various grades of cationic Guar gums as flocculants.

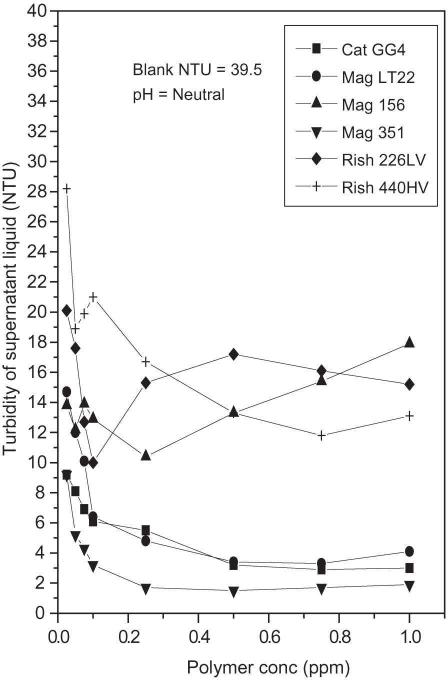

Figure 4.
Jar test result in silica suspension using Cat GG4 and commercial flocculants.

of flocculants was varied from 0.025 ppm to 1 ppm, calculated with respect to the total weight of the solution. The results are shown in Figs. 3–4.

Rheological Investigations

The rheological investigation was conducted in the laboratory using Controlled –Stress TA Instruments AR-1000 Advanced Rheometer. The temperature of the system was maintained 30°C throughout the experiments.

For rheological investigations, preparation of solution is very important. The aqueous solutions of guar gum (GG) and cationic Guar gum 4 (Cat GG4) were prepared by adding the required quantity of the polymers slowly to distilled water to avoid lumping and with continuous stirring by a magnetic stirrer at a temperature of 60°C. For guar gum and cationic guar gum, 0.5 wt% solutions were prepared. The results are shown in Figs. 5–6.

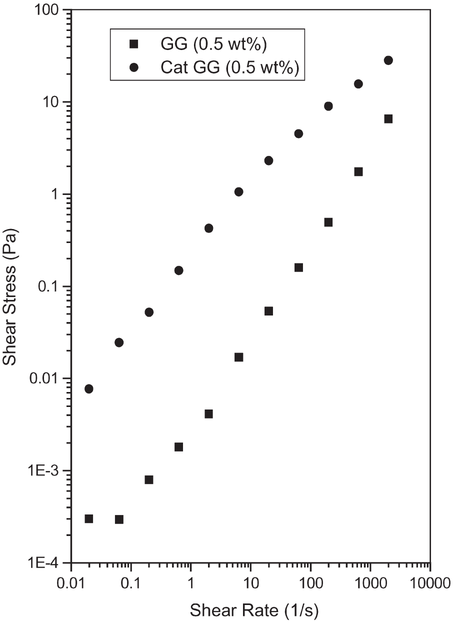

Figure 5.
Flow curves of 0.5 wt % of guar gum and cationic guar gum solution.

Discussion

Synthesis and Intrinsic Viscosity

Table 1 gives the details of synthetic parameters for the synthesis of various grades of cationic guar gums i.e. the series of Cat GG1, Cat GG2, Cat GG3, Cat GG4 and Cat GG5. Although a number of methods are available for incorporating a cationic moiety onto the backbone of polysaccharide, *N*- (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride has been preferred as a cationic moiety over recent years [19, 25]. It is because of the fact that guar gum is an effective backbone polymer for incorporating a cationic moiety using a quaternary ammonium compound.

From Table 1, it is clear that with increase in monomer concentration (from Cat GG1-Cat GG4), the intrinsic viscosity increases but with further increase in cationic monomer concentration, intrinsic viscosity decreases (Cat GG5), so at optimum monomer concentration, we achieved maximum intrinsic viscosity (Table 1). The optimum monomer concentration is also confirmed with respect to flocculation characteristics [26–28], which has been shown in Figure 3. The viscosity of polymer solution is considerably higher than that of the solvent. It is the function of hydrodynamic volume of the polymer in solution, which in turn, depends on the molecular weight of the polymer, its structure, the nature of the solvent, as well as the solution temperature. The longer the CHPTAC chain linked on backbone polymer, the higher is the intrinsic viscosity. In this study the intrinsic viscosity was graphically determined from the reduced and inherent viscosity (Figure 1). From Table 1, it is clear that the intrinsic viscosity of Cat GG4 is higher compared to others. The higher intrinsic viscosity of Cat GG4 is due to the longer CHPTAC chain present in Cat GG4.

Elemental Analysis

The results of element analysis of guar gum, all the grades of cationic guar gums and *N*- (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride are listed in Table 2. Guar gum does not show any significant presence of nitrogen. However, the negligible amount of nitrogen (0.16%) in guar gum is because of the presence of trace quantities of proteins in the commercial guar gum as it is evident from CHN analysis. It has been found that there is a considerable percentage of nitrogen in the cationic guar gums, which can be accounted for the presence of CHPTAC chain in the backbone of guar gum.

FTIR Analysis

The FTIR spectra of guar gum, cationic guar gum 4 and *N*- (3-chloro-2-hydroxypropyl) trimethyl ammonium chloride are shown in Figures 2.a, 2.b and 2.c respectively.

From figures, it is observed that in Cat GG4, there is one additional band present at 1397 cm^{-1}, which is assignable to C–N stretching vibration. Such band is absent in GG, which confirm the insertion of cationic moiety on guar backbone.

Flocculation Study

The flocculation performance of various grades of cationic guar gums was compared in 0.25 wt% silica suspensions. The result is shown in Figure 3. In this case, the turbidity of the supernatant liquid after flocculation was plotted against the polymer concentration. It is obvious from these results that Cat GG4, which contains longer CHPTAC chains (as evidence from the intrinsic viscosity value), is a better flocculant in silica suspension than that with the other cationic guar gums.

Afterwards the flocculation characteristics of Cat GG4 were compared with some of the commercially available flocculants in silica suspension (Figure 4), out of which some are cationic, some are nonionic and some are anionic in nature. From Figure 4, it is clear that only Magnafloc 351 (Mag 351) shows a better performance than Cat GG4, whereas Cat GG4 still shows better performance than the other commercial flocculants.

Rheological Investigations

The rheological studies of aqueous solutions of GG and Cat GG4 were carried out in 0.5-wt% solutions. We measured the shear rate, shear stress and shear viscosities of the aqueous solutions of the polymer samples by AR-1000 Advanced Rheometer. In steady state shear flow state, two main relationships of double logarithmic scales illustrate the rheological fingerprints of the samples under study. These are the flow behaviour curves (Fig. 5), showing the relationship between shear stress τ and shear rate γ and the viscosity curves (Fig 6) indicating the log-log plots of shear viscosity versus shear rate of aqueous solutions of the polysaccharides GG and Cat GG4. All the measurements are based on the assigned shear in CR (controlled rate) mode ranging from 0.028 to 2800 s^{-1}. Both aqueous solutions of GG and Cat GG4 show a strong pseudoplastic behaviour. In this case, shear stress increases with increase in shear rate and the polymer solutions show non-Newtonian behaviour.

The viscosity curve (Fig. 6) illustrates the variation of viscosity of aqueous solutions of polysaccharides (GG and Cat GG) with shear rate. The viscosity decreases with increase in shear rate, which is a strong proof of shear thinning behaviour of our polymer samples. This marked shear thinning behaviour of polysaccharide solutions may be explained by the conformational states of polymer molecules. It has been observed that the viscosity of the cationic guar gum solution increases compared to the base polysaccharide solution because of the presence of longer CHPTAC chain on the backbone of polysaccharides. As a mater of fact, the hydrodynamic volume of guar gum is lesser than that of cationic guar gum, so its solution viscosity is also lower over extended shear rate.

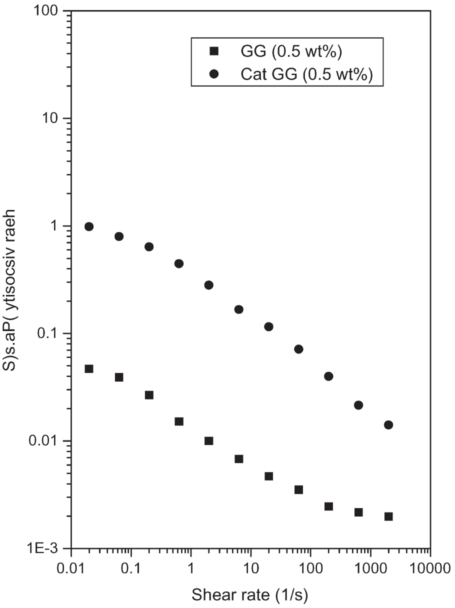

Figure 6.
Viscosity curves of guar gum and Cationic guar gum solution.

Conclusion

From the above experimental studies, it can be concluded that by incorporating a cationic moiety on the backbone of guar gum, naturally occurring polysaccharide, an effective flocculating agent can be developed for the treatment of wastewater, industrial effluent etc. The present results conclude the occurrence of loading of cationic moiety on the backbone of guar gum. Variation in the synthetic parameter results in a series of cationic guar gums with varying number and length of the CHPTAC chains resulted in different intrinsic viscosities. Investigation of FTIR spectra and elemental analysis provides a strong proof of cationization. Investigation on flocculation characteristics reveals that among the various grades of cationic guar gums, the one having longer CHPTAC chain, which is optimized one, performs better than those with shorter CHPTAC chains. When the best performing cationic guar gum was compared with some of the commercially available flocculants, it appears that our product surpasses all the commercial flocculants except only one. From the rheological investigations, it can be concluded that the aqueous solutions of both guar gum and its cationic counterpart exhibit the non-Newtonian pseudoplastic behaviour.

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