

# Characterization of Cationic Starch: An Efficient Flocculating Agent

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**ABSTRACT:** Starch is a known carbohydrate in which, regardless of its origin, two polysaccharides are found namely amylose and amylopectin. By insertion of a cationic moiety to the backbone of starch, a modified cationic starch can be developed which can be used as flocculant. Various grades of cationic starches were developed to optimize the best performing flocculant. The base polysaccharide, starch and the best performing cationic starch i.e., Cat St3 (which have been confirmed from flocculation characteristics and intrinsic viscosity measurement) have been characterized by various characterization techniques such as determination of molecular weight, elemental anal-

ysis, FTIR spectroscopy, intrinsic viscosity measurement, thermal analysis, etc. From the characterization, it could be concluded that there was a substantial incorporation of cationic moiety onto the backbone of starch. The flocculation efficacy of these cationized starches was compared with each other and with some of the commercial flocculants available in national and international market in manganese ore suspensions. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2674–2681, 2008

**Key words:** cationic; characterization; polysaccharide; starch and static light scattering analysis

## INTRODUCTION

There is a difficulty in the basic process of getting solid constituents out of a liquid solution or suspension. Fine particles with diameters on the order of 10  $\mu\text{m}$  will not settle out of suspension by gravity alone in an economically reasonable amount of time. Addition of flocculants to liquid suspensions causes aggregation of particles in so-called flocs, thereby increasing the ease of their removal. Since fresh water is a scarce commodity in many societies and a valuable one in all nations, reuse of industrial water and municipal sludges can have a powerful impact on the economy and environment. While water to be used for direct human consumption and for agriculture cannot be recycled, water used for industrial processes can be reused successfully if purified; and purification is dependent on getting the solid constituents out of suspension without imposing excessive cost.

Around the world, the application of synthetic flocculants is accepted for solid–liquid separation in the recycling of domestic wastewater and of industrial and mineral processing effluents.<sup>1–3</sup> Flocculation has played an important role in domestic and wastewater treatment, sludge dewatering, mineral benefi-

ciation,<sup>4–6</sup> etc. Flocculation is a process of bringing together smaller particles to form larger particles, often highly porous in nature.<sup>5,6</sup> The extensive use of polymers as flocculants is due to their distinct characteristic attributes.

An important member of the water-soluble polymers derived from natural process is starch. Starch is a mixture of two polymers of anhydroglucose units, amylose and amylopectin.<sup>7</sup> Amylose is the minor fraction with variation upto 25% depending upon source and amylopectin constitutes major fraction with variation upto 95%. Owing to its properties, starch has found application in pharmacy, cosmetics, therapeutics, papermaking, and the textile industry.<sup>8</sup> The development of the possibilities for applying this natural polymer is connected with the modification of its properties, among other things, by chemical modification.

Cationic polymerization is a technique for modifying the chemical and physical properties of synthetic and natural polymers. Applications of these modification reactions are useful in polymer chemistry. Synthetic polymers are much more effective than natural ones due to their versatile tailorability. However, they are not shear resistant. Natural polymers mainly polysaccharides are fairly shear stable, biodegradable, and cause flocculation at relatively higher concentration. It is thus evident that by developing a polymer composed of both natural and synthetic one, one can get the best properties of both.

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TABLE I  
Composition and Properties of Mn Ore Suspensions

Sample	% Mn	% Fe	% Al <sub>2</sub> O <sub>3</sub>	% SiO <sub>2</sub>	% P	% Moisture	Particle size (nm)	Sp. gravity (gm/cc)	Zeta potential (mV) at neutral pH
Mn Ore suspension	55	16	8	6	0.12	8	86.9	2.50	-32.0

We have seen that grafting synthetic polymers onto a polysaccharide backbone can result in an improved flocculant<sup>9</sup> as well as a better drag reducing agent.<sup>10</sup> Polyacrylamide-grafted polysaccharides are nonionic and therefore perform best in industrial effluents containing contaminant particles of relatively low negativity. Where colloidal particles are highly negatively charged, cationic polymers are more efficient.<sup>11</sup>

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.<sup>12</sup> Cationized polysaccharides are widely used as wet-end additives in papermaking.<sup>13</sup>

In our previous study,<sup>14</sup> the synthesis, part characterization, and flocculation properties of cationized starches in silica suspension had been carried out. This article deals with the synthesis, detailed characterization of various grades of cationic starches, and their application as flocculants in relation to manganese (Mn) ore suspensions.

## EXPERIMENTAL

### Materials

Materials for synthesis

Maize starch was supplied by E. Merck (India), Bombay, India. *N*-(3-Chloro-2-hydroxypropyl) trimethyl ammonium chloride (CHPTAC) was procured from Lancaster Synthesis Company, England. Analar (analytical grade) grade of sodium hydroxide was obtained from E. Merck (India), Bombay, India. Hydrochloric acid was purchased from E Merck (India), Bombay, India. S. D. Fine-Chem, India supplied isopropanol.

### Flocculants

Four commercial flocculants, namely Magnafloc LT 22 (Mag LT 22, 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) were used for comparison.

### Suspensions

The suspension used was manganese ore fines (gift sample from Joda Mines, Jharkhand, India). Details of the compositions are provided in Table I. Density was determined using a specific gravity bottle by the standard method. Particle size was determined with a Malvern 3601 Particle Size Analyzer (manufactured in England). Zeta potential was measured by Particle Micro Electrophoresis (Apparatus Mark II, manufactured in England) at pH = 7.0.

### Synthesis

Various grades of cationic starches were synthesized by inserting a cationic moiety *N*-(3-chloro-2-hydroxypropyl)-trimethyl ammonium chloride (CHPTAC) onto the polysaccharide (starch) backbone.<sup>14</sup> The reaction was carried out at a temperature that varied from 40 to 50°C. The details of synthesis parameters such as mole ratio of the reactants, reaction temperature, and time are given in Table II. The reaction proceeds as depicted in Scheme 1.

### Characterization

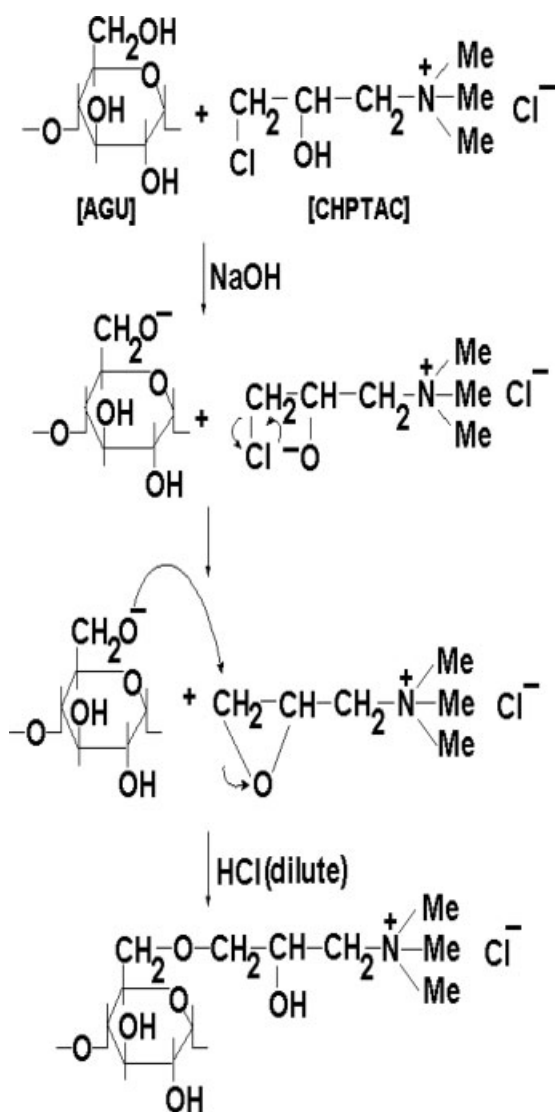
#### Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer

TABLE II  
Synthetic Details of Cationic Starch

Polymer	Amount of AGU <sup>a</sup> (mol)	Amount of CHPTAC (mol)	Volume of NaOH (mol)	Temp. (°C)	Time (h)	Intrinsic viscosity (dL/g)
Cat St1	0.0092	0.0039	0.015	40–50	18	7.5
Cat St2	0.0092	0.0053	0.015	40–50	15	8.0
Cat St3	0.0092	0.0066	0.015	40–50	18	8.8
Cat St4	0.0092	0.0079	0.015	40–50	18	8.2
St	–	–	–	–	–	1.25

<sup>a</sup> Calculated on the basis of Anhydroglucose unit (AGU). One mole AGU = 162 g.



**Scheme 1** Schematic representation for the synthesis of cationic starch.

(CS/S: 0.003899) at 25°C. The viscosities were measured in dilute aqueous solution. The pH of the aqueous solution was neutral. The time of flow for solutions was measured at four different concentrations.

From the time of flow of polymer solutions ( $t$ ) and that of the solvent ( $t_0$ , for distilled water), relative viscosity ( $\eta_{rel} = t/t_0$ ) was obtained. Specific viscosity was calculated from the relation  $\eta_{sp} = \eta_{rel} - 1$ . Then, the reduced viscosity ( $\eta_{sp}/C$ ), and the inherent viscosity ( $\ln \eta_{rel}/C$ ) were calculated, where  $C$  is the polymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots,<sup>15</sup> i.e.,  $\eta_{sp}/C$  versus  $C$  and  $\ln \eta_{rel}/C$  versus  $C$ , to zero concentration. The intrinsic viscosity values of starch and various grades of cationized starches are listed in Table II.

#### Determination of weight average molecular weight

The weight average molecular weight ( $M_w$ ) and the mean square radius of gyration ( $S_z^2$ ) of starch (St) and various grades of cationic starches were determined by static light scattering (SLS) analysis using DLS-7000 Super Dynamic Light Scattering Spectrophotometer. The results are given in Table III.

#### Elemental analysis

Elemental analysis of starch, cationized starches, and CHPTAC was performed with a Carlo Erba 1108 elemental analyzer. The estimation of only three elements, that is, carbon, hydrogen, and nitrogen was undertaken. The results are shown in Table IV.

#### 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 values for starch, various grades of cationic starches, and CHPTAC are summarized in Table V.

#### Thermal analysis

The thermal analysis of all the samples (i.e., starch, CHPTAC, and Cat St3) was carried out with Stanton

**TABLE III**  
Characterization of Flocculants in Mn Ore Suspensions

Polymer	Wt. average mol. Wt. ( $M_w$ ) (g/mol)	$R_G$ (nm)	Settling velocities in Mn ore suspensions (cm/s)
Starch	1.07E + 05	10.1	0.46
Cat St1	3.97E + 05	18.2	0.66
Cat St2	4.20E + 05	20.1	0.70
Cat St3	4.33E + 05	21.5	0.76
Cat St4	4.26E + 05	21.0	0.72
Mag LT 22	4.76E + 05	97.5	0.83
Mag 156	6.56E + 05	91.9	0.60
Rish 226 LV	3.27E + 05	95.6	0.51
Rish 440 HV	1.16E + 05	11.6	0.58

TABLE IV  
Elemental Analysis Results of Starch, Cationic Starches, and CHPTAC

Polymer	% of carbon	% of hydrogen	% of nitrogen	Degree of substitution (DS)
St	39.31	6.36	0.12	–
CHPTAC	37.71	7.82	7.34	–
Cat St1	39.66	6.64	2.85	0.37
Cat St2	39.24	6.42	3.22	0.42
Cat St3	39.54	6.53	3.82	0.50
Cat St4	39.36	6.57	3.68	0.48

Redcroft (STA 625) Thermal analyzer. Thermo gravimetric analysis (TGA and DTG) was performed up to a temperature of 600°C, starting from room temperature in an atmosphere of nitrogen. The heating rate was uniform in all cases at 10°/min. The TGA and DTG curves are shown in Figures 1 and 2, respectively.

#### X-ray diffractometry

Powder samples of the polymers were subjected to XRD. PW 1840 and PW 1729 X-ray generator (Phillips, Holland) were used for this study using CuK $\alpha$  radiation. The scattering angle (2 $\theta$ ) was varied from 10° to 45°. The XRD curve is shown in Figure 3.

#### Flocculation efficacy

Flocculation efficacy was determined by a comparison of settling velocities. The settling test was conducted in a 100 mL stoppered graduated cylinder, and settling times were recorded with a stopwatch. First, the cylinder was filled with the suspension sample and then the polymer flocculant was added to it. Polymer concentration was 9 ppm for Mn ore suspensions. The cylinder was inverted 10 times for thorough mixing. Afterward, the cylinder was set upright and the height of interface between water and the settling solid bed was measured over time. Interface height of the flocculant-containing suspension of Mn ores was measured as a function of time and plotted (Figs. 4 and 5). The slopes of the linear

portion give the settling velocities in cm · s<sup>-1</sup> (Table III).

## DISCUSSIONS

### Synthesis and intrinsic viscosity

There are number of methods available for incorporating a cationic moiety onto the backbone of polysaccharide, CHPTAC has been preferred as a cationic moiety over recent.<sup>16,17</sup> It is because of the fact that starch is an effective backbone polymer for grafting a cationic moiety using a quaternary ammonium compound.

Table II shows the synthetic details of the cationic polymers based on starch. A series of four cationic starches were synthesized. From Table II, it is clear that with increase in monomer concentration (from Cat St1 to Cat St3) the intrinsic viscosity increases but after optimum monomer concentration, with further increase in monomer concentration, intrinsic viscosity decreases (Cat St4). The optimum monomer concentration is with respect to flocculation characteristics.<sup>14,18</sup>

### Weight average molecular weight and radius of gyration

The weight average molecular weights ( $M_w$ ) and the radius of gyration  $R_G$  of starch and various grades of cationic starches were determined from Zimm Plot by Static Light Scattering analysis using a DLS-7000 Super Dynamic Light Scattering Spectrometer

TABLE V  
FTIR Values of Starch, Cationic Starches, and CHPTAC

Polymer	–OH stretching (cm <sup>-1</sup> )	–CO stretching (cm <sup>-1</sup> )	–CH stretching (cm <sup>-1</sup> )	–CN stretching (cm <sup>-1</sup> )	CH <sub>2</sub> –O–CH <sub>2</sub> stretching (cm <sup>-1</sup> )	C–Cl adsorption band (cm <sup>-1</sup> )
Starch	3328	1152	2907	–	1089, 1008	–
CHPTAC	3445	–	2910	1400	–	675
Cat St 1	3340	1160	2908	1398	1080, 1010	–
Cat St 2	3327	1157	2924	1408	1094, 1012	–
Cat St 3	3330	1161	2916	1404	1089, 1000	–
Cat St 4	3335	1164	2905	1402	1085, 1005	–

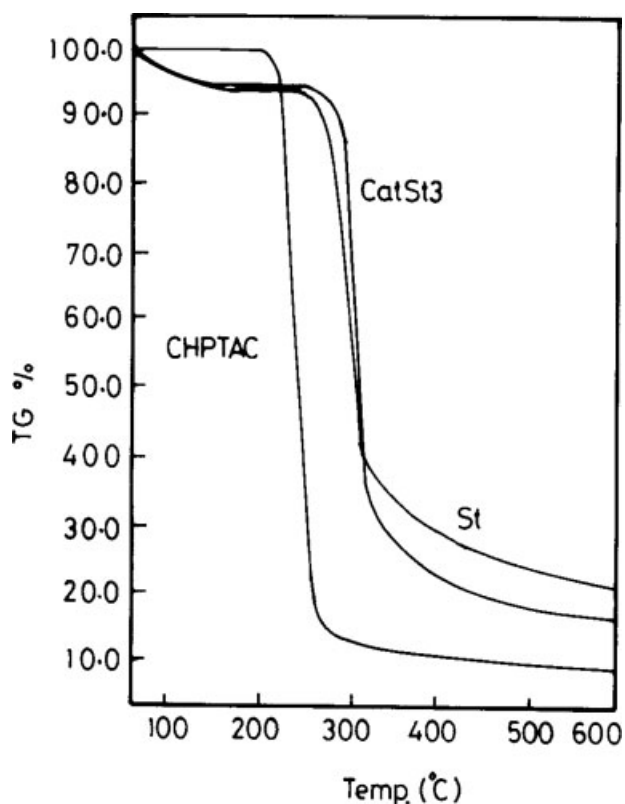


Figure 1 TGA curves of starch, Cat St3, and CHPTAC.

(Otsuka Electronics, Hirakata-City, Osaka, Japan). The results are summarized in Table III. From Table III, it is obvious that the weight average molecular

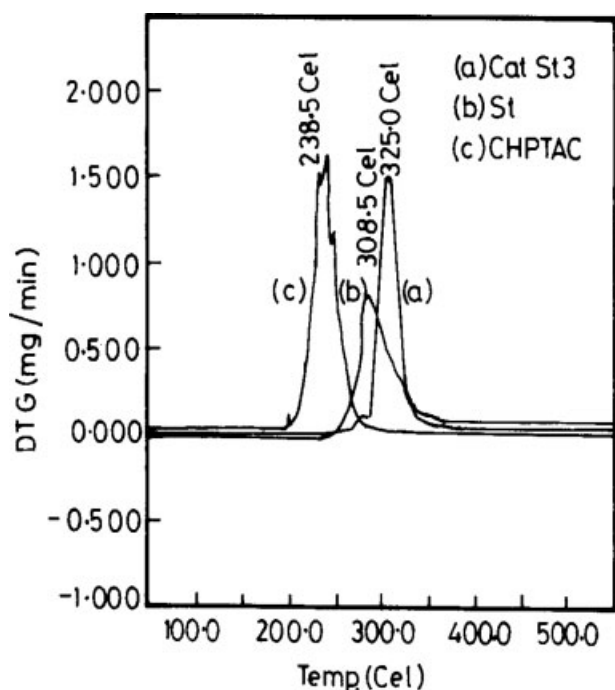


Figure 2 DTG curves of starch, Cat St3, and CHPTAC.

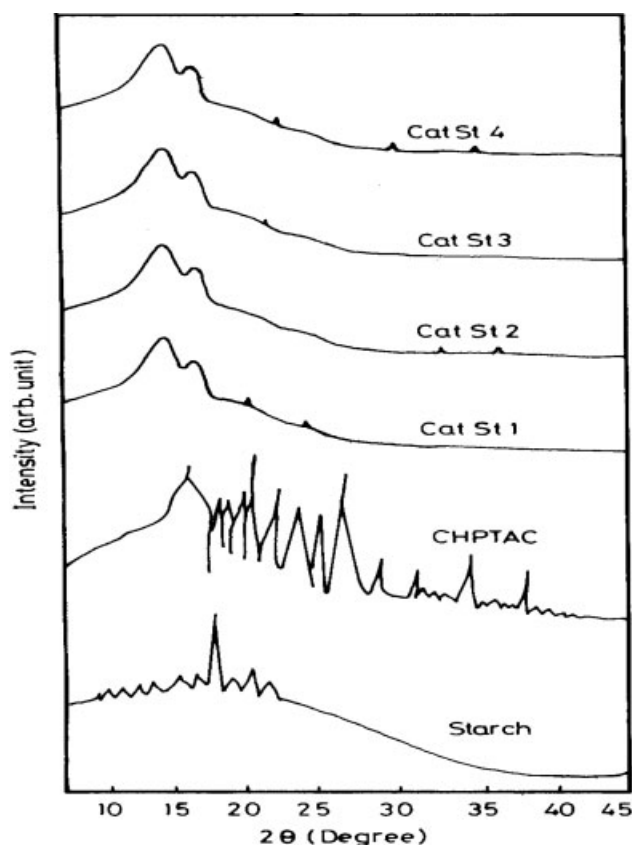


Figure 3 XRD spectrum of (a) starch, (b) CHPTAC, and (c) Cat St3.

weights ( $M_w$ ) of all the grades of cationic starches are higher than that of starch, because of the presence of inserted CHPTAC chain on the backbone of starch. When compared amongst the various grades of cationic starches, it has been found that Cat St3, which is optimized one with respect to flocculation characteristics (Fig. 3), is having highest molecular weight compared to others.

Radius of gyration is a parameter, which characterizes the size of a particle of any shape. The higher the radius of gyration  $R_G$ , molecular dimension of the polymer will be more and that will affect the flocculation characteristics synergistically.  $R_G$  values were obtained using the procedure developed originally by Bruno Zimm<sup>19</sup> and described by Gedde.<sup>19</sup>  $R_G$  is nothing but a measure of pervaded volume of a polymer. The higher is the pervaded volume, the higher will be the  $R_G$ . Since insertion of cationic moiety onto the polysaccharide backbone enlarges the pervaded volume and thus increases the radius of gyration, which has been observed in the result as presented in Table III.

Recently, a relationship has been established between the settling velocity  $y$  and  $R_G$ .<sup>20</sup> Namely, there is a one-to-one correspondence in the form of a power law relationship:

$$y = aR_G^b \quad (1)$$

where 'a' and 'b' are parameters characteristic for a given suspension medium, that is both the dispersed phase and the majority liquid phase.

### Elemental analysis

The results of element analysis of starch, all the grades of cationic starches and CHPTAC are listed in Table IV. Starch does not show any significant presence of nitrogen. However, the negligible amount of nitrogen (0.12%) in starch is because of the presence of trace quantities of proteins in the commercial starch as it is evident from CHN analysis. It has been found that there is a considerable percentage of nitrogen in the cationic starches, which can be accounted for the presence of CHPTAC chain in the backbone of starch. In the series of cationic starches, the variation in the nitrogen content, although not much, is significant in case of Cat St3. So, it appears that CHPTAC moieties are incorporated in greater extent with increase in its concentration, possibly through participation of larger number of —OH groups of starch in covalent linkages.

Degree of substitution (DS) has been calculated based on Kjeldahl analysis.<sup>21</sup>

$$DS = \frac{\% \text{ of N in the cationic polysaccharide} - \% \text{ of N in the polysaccharide}}{\% \text{ of N in CHPTAC}} \quad (2)$$

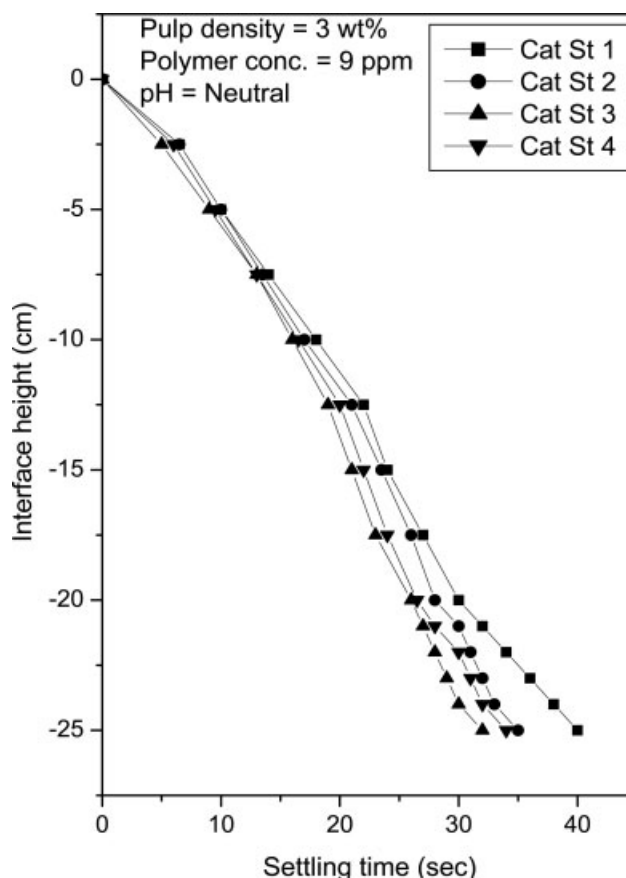
It is clear from the Table IV that Cat St 3 has the highest degree of substitution amongst the four cationic starches.

### FTIR spectroscopy

The FTIR values of starch, various grades of cationic starches, and CHPTAC are summarized in Table V. From Table V, it is observed that in cationic starch, there is one additional band present in the range of 1398–1410  $\text{cm}^{-1}$ , which is assignable to C—N stretching vibration. Such band is absent in starch, which confirms the insertion of cationic moiety on starch backbone.

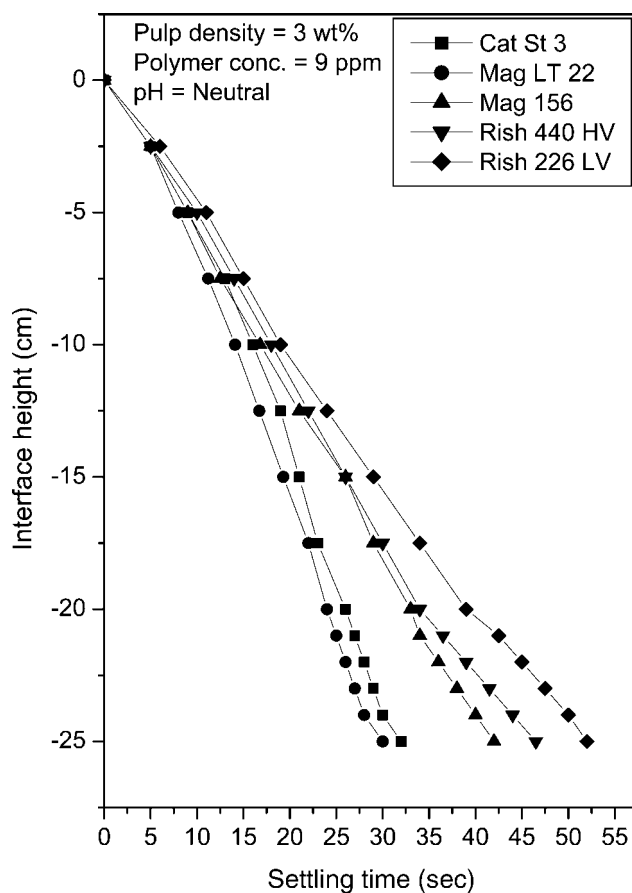
### Thermal analysis (TGA)

The TGA and DTG thermo grams of starch, Cat St3, and CHPTAC obtained at scan rate of 10°C/min in



**Figure 4** Settling characteristics of cationic starches in Mn ore suspension.

nitrogen atmosphere are shown in Figures 1 and 2, respectively. In case of starch (Fig. 1), two distinct zones are observed where the weight is being lost. The initial weight loss is due to the presence of small amount of moisture in the sample. The second zone of weight loss is observed when the polymer decomposition takes place. The rate of weight loss is increased with increase in temperature. In case of Cat St3, the degradation of the polymer takes place in two stages. The first decomposition is for the degradation of both starch and CHPTAC. The second degradation is due to the decomposition of the cyclised product. From the TGA curve, it is obvious that Cat St3 is thermally more stable as compared to starch. So, from the TG results, we conclude that the incorporation of CHPTAC chains onto the starch backbone enhances the thermal stability of the starch. The DTG curve (Fig. 2) further helps in understanding the weight losses with increase in



**Figure 5** Settling characteristics of Cat St3 compared to that of commercial flocculants in Mn ore suspensions.

temperature. Here, also it is observed that the Cat St 3 undergo thermal degradation at higher temperatures compared to the base polysaccharide.

### X-ray diffraction (XRD) analysis

Figure 3 shows the X-ray analysis of starch, CHPTAC, and various grades of cationic starches. From the figure, it is obvious that starch exhibits a very small crystallinity. However, the cationic products do not have any peak showing crystallinity. Again the sharp peaks found in CHPTAC monomer are also absent in the cationic product. The result elucidates that the crystalline structure was changed to some extent owing to introduction of CHPTAC to starch.

### Flocculation characteristics

The flocculation efficacies of various cationic starches and the best performing cationic starch (i.e., Cat St 3) with the commercial flocculants in a Mn ore suspension are shown in Figures 4 and 5. Cat St3 has

the highest settling velocity among the various cationized starches. It performs well also compared to commercial flocculants; one of these (Mag LT 22) has a higher settling velocity. Numerical values for the settling velocities for the various flocculants are reported in Table III.

### CONCLUSION

The aim of this study was to prove the grafting of cationic moiety on the backbone of starch. The present results conclude the occurrence of loading of cationic moiety on the backbone of starch. Variation in the synthetic parameter results in a series of cationic starches 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. From SLS analysis, it is obvious that because of the presence of CHPTAC chains on the starch backbone, the molecular weight enhanced in case of cationic starch. TGA and DTG results showed different thermal decomposition patterns for the virgin polysaccharide and the cationic polysaccharide.

XRD patterns showed that the crystalline structure was changed to some extent owing to introduction of CHPTAC to starch. Further, we have shown that a modified polysaccharide (cationic starch) developed by us performs almost as well as or better than commercial flocculants in suspension containing a large degree of negatively charged particles.

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