

# Synthesis and Characterization of Cationic Guar Gum: A High Performance Flocculating Agent

Sagar Pal,<sup>1</sup> D. Mal,<sup>2</sup> R. P. Singh<sup>3</sup>

<sup>1</sup>Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana

<sup>2</sup>Department of Chemistry, Indian Institute Technology - Kharagpur, Kharagpur 721 302, West Bengal, India

<sup>3</sup>Vice-chancellor, University of Lucknow, Lucknow 226 007, Uttar Pradesh, India

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**ABSTRACT:** Among various water-soluble polysaccharides, guar gum is one of the most important polysaccharide, which is having a wide variety of applications. By grafting a cationic moiety onto the backbone of guar gum, a modified naturally occurring polysaccharide can be developed, which used to be use as high performance flocculating agent and viscosifier (Singh et al.).<sup>15</sup> Various grades of cationic guar gums have been synthesized by varying the synthesis parameters. All these polysaccharides have been characterized by various characterization

techniques, such as elemental analysis, FTIR spectroscopy, intrinsic viscosity measurement, molecular weight determination, thermal analysis, and X-ray diffraction analysis. From all of these characterization studies, it has been confirmed that the cationic moiety has been grafted onto the backbone of polysaccharide. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 3240–3245, 2007

**Key words:** cationic; characterization; flocculant; guar gum; SLS analysis

## INTRODUCTION

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. The world's current crisis of potable water necessitates the treatment of municipal wastewater and industrial effluents under water recycling paradigm. Under the earlier treatment, the contaminants are flocculated by organic and inorganic chemicals for liquid/solid separation. Flocculation plays an important role in domestic and wastewater treatment, sludge dewatering, and mineral beneficiation,<sup>1,2</sup> etc. Flocculation<sup>3,4</sup> 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 because of their distinct characteristic attributes.

In the authors' laboratory, many graft copolymers have been synthesized by grafting polyacrylamide

(PAM) onto starch,<sup>5</sup> Carboxymethyl cellulose,<sup>5</sup> guar gum (GG),<sup>6</sup> xanthan gum,<sup>7</sup> etc. It has been observed that the graft copolymers having fewer but longer PAM branches are fairly shear stable and exhibit better flocculation and drag reducing characteristics.<sup>8</sup> But these graft copolymers are nonionic in nature and are effective flocculant in relatively low negatively charged suspensions. But for highly negatively charged suspensions, cationic flocculants are most effective.

Among various water-soluble polysaccharides, GG is one of the most important polysaccharide, which is having a wide variety of applications. GG is the endosperm polysaccharide of the seed of *Cyamopsis tetragonoloba*, which belongs to the *Luguminosoe* family.<sup>9</sup> It is a galactomannan (Fig. 1) consisting of backbone of  $\alpha$ -1,4-D-mannopyranosyl units, with every second unit bearing a  $\beta$ -1,6-D-galactopyranosyl unit.<sup>10,11</sup> It is easily available and cheap. India is the largest exporter of GG in world.

Cationised polysaccharides are effective flocculants over a wide range of pH. They are nontoxic and easily biodegradable. They are widely used as wet-end additives in papermaking,<sup>12</sup> used for controlled flocculation, retention, and paper strength.<sup>13,14</sup>

The cationic moieties have been grafted on various polysaccharides; however no attempt has been made to develop various grades of cationic guar gums (Cat GG4), which are effective flocculants. In our previous study,<sup>15</sup> we carried out synthesis, partial characterization, flocculation characteristics,

Correspondence to: S. Pal (pal\_sagar2001@yahoo.com).

Present address: Department of Applied Chemistry, Birla Institute of Technology (B. I. T.), Mesra, Ranchi 835 215, Jharkhand, India.

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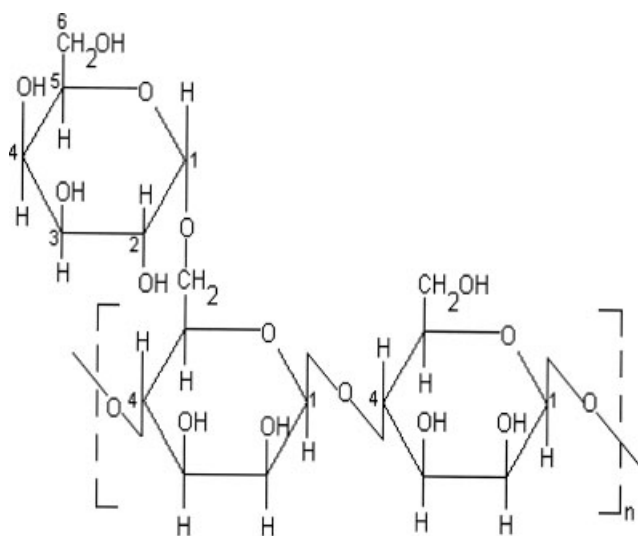


Figure 1 Structure of Guar gum.

and rheological investigations of the synthesized Cat GG4. Because the molecular attributes of cationic polymers play an important role in the flocculation and rheological phenomenon, proper characterization is essential. This article reports on the detailed characterization of cationised guar gum.

## EXPERIMENTAL

### Materials

GG was a gift sample by Hindustan Gum and Chemicals, Bhiwani, Haryana, India. *N*-(3-Chloro-2-hydroxypropyl)-trimethyl ammonium chloride (CHPTAC) was procured from Lancaster Synthesis, England. Analar (analytical grade) grade of sodium hydroxide was obtained from E. Merck, Bombay, India. Hydrochloric acid was purchased from E. Merck (India). S. D. Fine-Chem, India supplied Isopropanol.

### Synthesis

Various grades of Cat GG4 have been synthesized by grafting a cationic moiety CHPTAC onto the

polysaccharide backbone. The details of the synthesis and the reaction conditions are as follows—

Aqueous solution of GG was prepared by dissolving the required amount of polysaccharide in water at room temperature by constant stirring for about 30 min. A mixture of CHPTAC and aqueous sodium hydroxide was added to GG solution. The reaction was then continued for several hours. After that dilute hydrochloric acid was added for lowering the pH below seven to stop the cationization process.<sup>16</sup> 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 h. The details of synthesis parameters, such as mole ratio of the reactants, reaction temperature, and time, are given in Table I.

## Characterization

### Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde 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,<sup>17</sup> which is a standard procedure for measurement of intrinsic viscosity with an Ubbelohde viscometer. The time of flow for solutions was measured at four different concentrations. From the time of flow of polymer solution ( $t$ ) 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>18</sup> i.e.,  $\eta_{sp}/C$  versus  $C$  and  $\ln \eta_{rel}/C$  versus  $C$ , to zero concentration.

The intrinsic viscosity values of GG and various grades of cationised guar gums are listed in Table I.

TABLE I  
Synthesis Details of Cationic Guar Gum

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 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

**TABLE II**  
Molecular Weight and Radius of Gyration Result of GG and Cat GG4

Polymer	Wt. average mol. wt. ( $M_w$ )	Radius of gyration ( $S_z^2$ )
GG	1.163E+005	3.160E+002A
Cat GG4	6.604E+005	4.400E+002A

Determination of weight average molecular weight

The weight average molecular weight ( $M_w$ ) and the mean square radius of gyration ( $S_z^2$ ) of GG and the optimized Cat GG4, which has been confirmed from intrinsic viscosity and flocculation characteristics<sup>15</sup> were determined by static light scattering (SLS) analysis, using DLS-7000 Super Dynamic Light Scattering Spectrophotometer. The results are given in Table II.

Elemental analysis

Elemental analysis of GG, Cat GG4, 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 result is shown in Table III.

FTIR Spectroscopy

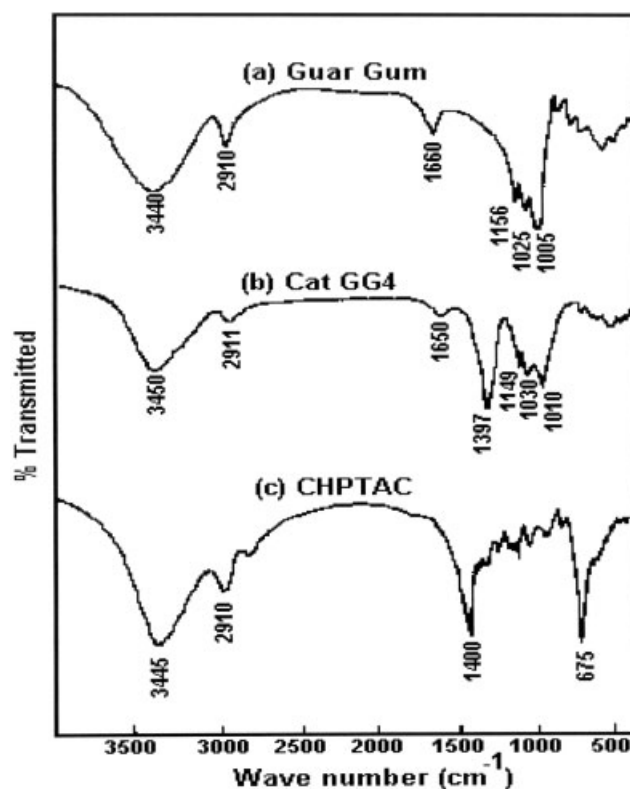
A Thermo Nicolet FTIR Spectrophotometer (Model-Nexus 870 FTIR) was used and the potassium bromide (KBr) pellet method used for FTIR study. The FTIR spectra of GG, Cat GG4, and CHPTAC are shown in Figure 2(a-c), respectively.

Thermal analysis

The thermal analysis (TGA/DTG) of GG, Cat GG4, and CHPTAC was carried out with Stanton Redcroft (STA 625) Thermal analyzer. TGA analysis of the samples was performed upto a temperature of 600°C, starting from room temperature in an atmosphere of

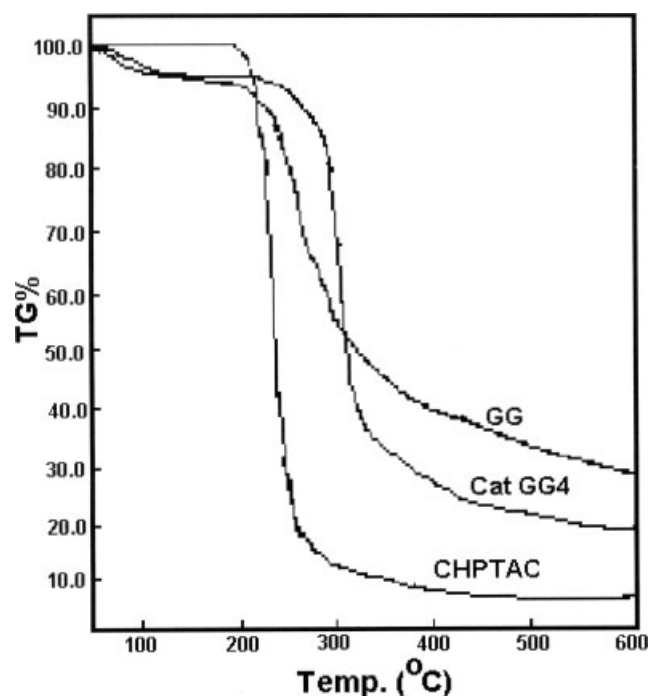
**TABLE III**  
Elemental Analysis Result of Various Grades of Cationic Guar Gums

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

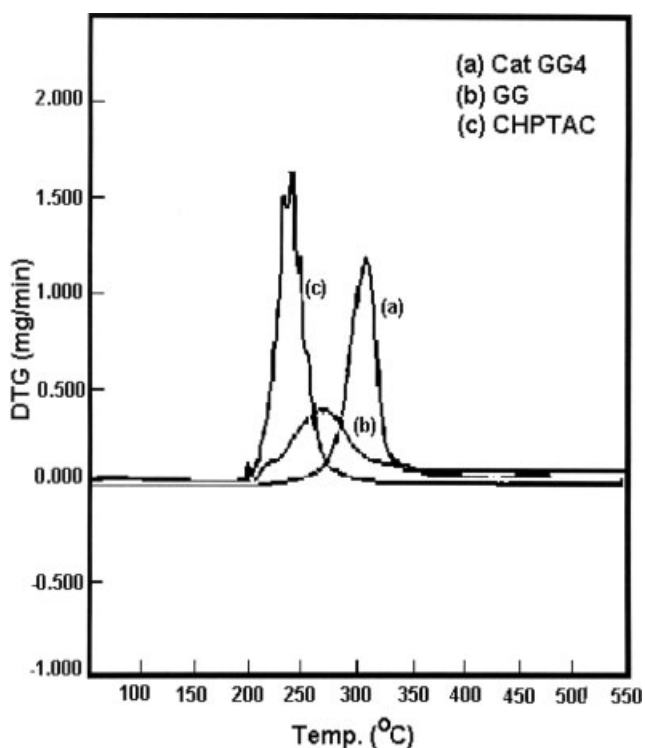


**Figure 2** FTIR spectrum of (a) GG, (b) Cat GG4, and (c) CHPTAC.

nitrogen. The heating rate was uniform in all cases at 10 deg/min. The TGA and DTG curves are shown in Figures 3 and 4.



**Figure 3** TGA curve of GG, Cat GG4, and CHPTAC.



**Figure 4** DTG curve of (a) Cat GG4, (b) GG, and (c) CHPTAC.

#### X-ray diffraction analysis

GG, CHPTAC and Cat GG4 were used for X-ray diffraction (XRD) analysis. The powder polymer sample was packed into a hole of 2 mm in diameter in a small container made of perspex [poly(methyl methacrylate)] about 1.5 mm thick. This piece was mounted on the specimen holder with pressure-sensitive tape so that the X-ray beam passed through the hole. A PW 1840 diffractometer and PW 1729 X-ray generator (Philips, Holland) were used for this study to produce Cu  $K\alpha$  radiation. The results are shown in Figure 5(a–c).

#### Synthesis and intrinsic viscosity

Table I gives the details of synthesis parameters for the synthesis of various grades of Cat GG, 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, CHPTAC has been preferred as a cationic moiety over recent years.<sup>19,20</sup> It is because of the fact that GG is an effective backbone polymer for grafting a cationic moiety, using a quaternary ammonium compound.

Table I shows the synthesis details of the cationic polymers based on GG. A series of five Cat GG4

were synthesized. From Table I, it is clear that with increase in monomer concentration (from Cat GG1–Cat GG4) the intrinsic viscosity increases but after optimum monomer concentration, with further increase in monomer concentration, intrinsic viscosity decreases (Cat GG5). The optimum monomer concentration is with respect to flocculation characteristics.<sup>15,21,22</sup> 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. From Table I, it is clear that the intrinsic viscosity of Cat GG4 is higher when compared with others. The higher intrinsic viscosity of Cat GG4 is due to the longer CHPTAC chain present in Cat GG4.

#### $M_w$ and radius of gyration

The  $M_w$  and the radius of gyration of GG and the best performing Cat GG4 were determined from Zimm Plot, using SLS analysis. SLS measures the intensity of light scattered off of a solution at a single time. In 1948, Zimm derived the relationship between the concentration and the intensity of the scattered light.

$$K [C/I] = 1/MP(\theta) + 2A_2c$$

where  $c$  is the concentration,  $M$  is the solute molecular weight,  $P(\theta)$  is the particle scattering function that depends on particle shape, and  $I$  is the intensity of scattered light.<sup>23</sup> The constant  $K$  is defined to be

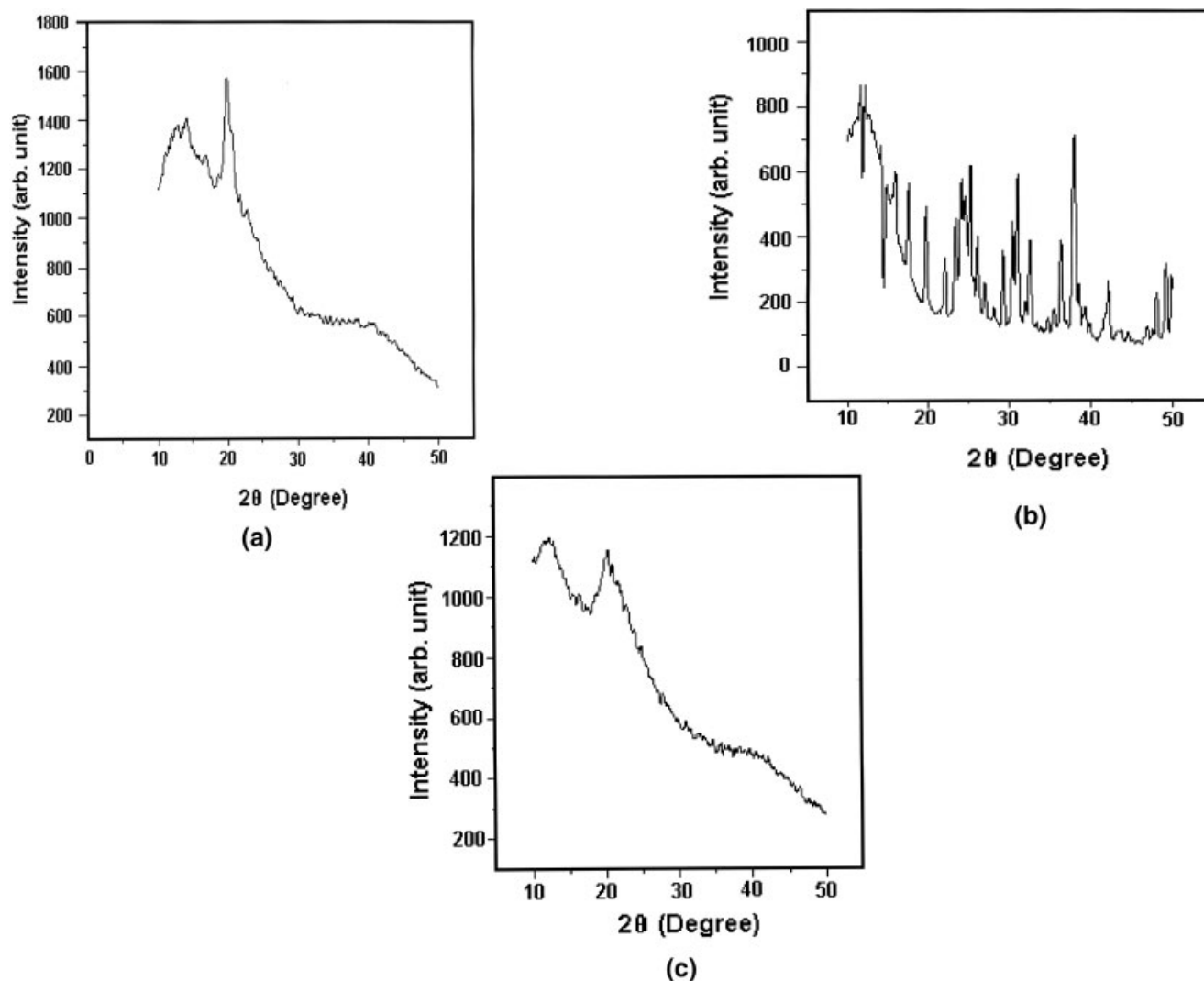
$$K = 4\pi^2 n^2 (dn/dc)^2 N_A^{-1} \lambda_0^{-4}$$

where  $n$  is the index of refraction,  $dn/dc$  is the refractive index increment, and  $\lambda_0$  is the wavelength of the incident light.<sup>24</sup> Zimm then proposed the use of a special graphing technique, now called a Zimm plot. A Zimm plot graphs the concentration over the intensity versus  $\sin^2(\theta/2)$ .<sup>23</sup>

Before constructing a Zimm plot, counts per second must be converted to reduced Rayleigh ratios using the expression—

$$R_0 = R_c(90^\circ) \sin(\theta) (I_\theta/I_c)$$

where  $R_c(90^\circ)$  is the absolute scattering intensity of toluene,  $I_\theta$  is the experimental intensity corrected by the Brookhaven software, and  $I_c$  is the corrected experimental intensity of toluene at  $90^\circ$ .<sup>25</sup> In this experiment, Zimm plots are fit using both linear and quadratic functions<sup>26</sup> of  $c/R_\theta$  versus scattering



**Figure 5** XRD spectrum of (a) GG, (b) CHPTAC, and (c) Cat GG4.

vector  $q^2$ . These fits are used to extrapolate  $c/R_\theta$  to zero scattering angle to get a value  $c/R_0$ . The  $M_w$  is then determined using a virial expansion—

$$K_c/R_\theta = 1/M_w(1 + 2A_2M_w c + 3A_3M_w c^2 + \dots)$$

where all the virial coefficients ( $A_2$ ,  $A_3$ , etc.) higher than second order are ignored to give a linear relationship.<sup>27</sup>

The results are summarized in Table II. From Table II, it is obvious that the  $M_w$  of Cat GG4 is higher than that of GG, because of the presence of inserted CHPTAC chain on the backbone of GG.

Radius of gyration is a parameter, which characterizes the size of a particle of any shape. The higher the radius of gyration, molecular dimension of the polymer will be more and that will affect the flocculation characteristics synergistically. From the radius of gyration results (Table II), it has been found that Cat GG4 has higher  $S_z^2$  value when com-

pared with GG, which also affects the flocculation performance.<sup>15</sup>

#### Elemental analysis

The results of element analysis of GG, all the grades of Cat GG4 and CHPTAC are listed in Table III. GG does not show any significant presence of nitrogen. However, the negligible amount of nitrogen (0.12%) in GG is because of the presence of trace quantities of proteins in the commercial GG as it is evident from CHN analysis. It has been found that there is a considerable percentage of nitrogen in the Cat GG4, which can be accounted for the presence of CHPTAC chain in the backbone of GG. From the element analysis (Table III), 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 GG in covalent linkages.

### FTIR Spectroscopy

The FTIR spectra of GG, Cat GG4, and CHPTAC are shown in Figure 2(a–c), respectively.

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

### Thermal analysis

The TGA curve of GG, Cat GG4, and CHPTAC are shown in Figure 3. In case of GG (Fig. 3), 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 GG4, the degradation of the polymer takes place in one stage. The decomposition is due to the degradation of both GG and CHPTAC and also because of the decomposition of the cyclised product. From the TGA curve, it is obvious that Cat GG4 is thermally more stable as compared with GG. So, from the TG results, we conclude that the incorporation of CHPTAC chains onto the guar backbone enhances the thermal stability of the GG because of the increased electrostatic attraction between the chains overcoming the mutual repulsion of positive charges of the loaded cationic moiety.

The DTG curve (Fig. 4) further helps in understanding the weight losses with increase in temperature. Here, also it is observed that the Cat GG4 undergo thermal degradation at higher temperatures when compared with the base polysaccharide.

### XRD analysis

Figure 5(a–c) show the X-ray analysis of GG, CHPTAC, and Cat GG4, respectively. From Figure 5(a), it is obvious that GG exhibits a very small crystallinity. However, the cationic product [Fig. 5(c)] does not have any peak showing crystallinity. Again the sharp peaks found in CHPTAC monomer [Fig. 5(b)] are also absent in the cationic product. The absence of the crystallinity peaks in case of Cat GG4 may be due to the disruption of crystalline structure by the inserted CHPTAC chains.

### CONCLUSIONS

The aim of this study was to prove the occurrence of cationization in the backbone of GG. From the characterization studies, it is being confirmed that the cationic moiety has been grafted onto the guar gum backbone, resulting in a formation of a modified naturally occurring polysaccharide, Cat GG4.

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