

# Synthesis and Characterization of Grafted Carboxymethyl Guar Gum

P. Adhikary,<sup>1</sup> S. Krishnamoorthi,<sup>1</sup> R. P. Singh<sup>2</sup>

<sup>1</sup>Department of Chemistry, Banaras Hindu University, Varanasi 221005, India

<sup>2</sup>Emeritus Scientist Indian Institute of Science Education and Research, Pune 411021 India

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**ABSTRACT:** Graft copolymers of carboxymethyl guar gum (CMGG) and polyacrylamide (PAM) have been synthesized by grafting polyacrylamide chains onto carboxymethyl guar gum backbone using a ceric-ion-induced solution polymerization technique. By varying the amount of initiator, three different grades of graft copolymers are synthesized. The characterization of graft copolymer is carried out by FTIR, NMR, intrinsic viscosity measurement,

SEM, SLS, DTG, and rheology. A comparison of flocculation efficiency of CMGG and its graft copolymer shows that the graft copolymer exhibits better flocculation performance. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2621–2626, 2011

**Key words:** graft copolymer; carboxymethyl guar gum; polyacrylamide

## INTRODUCTION

Carboxymethyl guar gum (CMGG) is an anionic semisynthetic guar gum derivative. The polysaccharide backbone is similar to guar gum which is a galactomannan. It is prepared by reacting guar gum with sodium monochlorate in the presence of sodium hydroxide.<sup>1</sup>

Carboxymethyl guar gum (CMGG) is a cheap and easily water soluble commercial polysaccharide. In this case CMGG has been chosen as backbone polysaccharide and PAM branches have been grafted on it. The structure of carboxymethyl guar gum is given in Figure 1.

Grafting is an important procedure to obtain suitably modified polymers, which combines the properties of both natural and synthetic polymers.<sup>2,3</sup> The great advantages thus obtained are high flocculation efficiency, controlled biodegradation and shear resistance characteristics of the developed graft copolymers.<sup>4–6</sup> Various types of graft copolymers have been synthesized by grafting polyacrylamide onto various polysaccharides like amylopectin, cashew gum, guar gum, hydroxypropyl guar gum, dextran, glycogen etc. backbone.<sup>7–12</sup> It has been observed that these graft copolymers exhibit better flocculation characteristics in various suspensions than the PAM-based linear polymers. The better

efficiency of these graft copolymers over those of the linear PAM can be attributed to the better approachability of the grafted PAM chains to the colloidal particles than the linear polymers, as proposed by Singh.<sup>13–15</sup>

Ceric ion has been used to initiate graft copolymerization of many monomers on various substrates.<sup>16–18</sup> Grafting is generally considered to result from propagation of radical sites generated on polymeric substrates and therefore minimizes the formation of homopolymer. This article examines some aspects of synthesis, and characterization of PAM grafted CMGG (CMGG-g-PAM). This article also examines the flocculating efficiency of the synthesized products.

## EXPERIMENTAL

### Materials

Carboxymethyl guar gum is procured from HICHEM, Bhiwani, India. Acrylamide is procured from E. Merck, Germany. Ceric ammonium nitrate (CAN) is obtained from Loba Chemie, Mumbai, India. Acetone of laboratory grade is obtained from E Merck, Bombay, India and hydroquinone is obtained from S.D Fine Chemicals, Mumbai, India. CMGG is subjected to soxhlet extraction for further purification. Acrylamide, CAN, acetone, and hydroquinone are used without further purification.

### Purification of gum

Natural polysaccharides contain some nonpolysaccharide ingredients like proteins, fats, fibers, and

Correspondence to: P. Adhikary (dr.pubali@gmail.com).  
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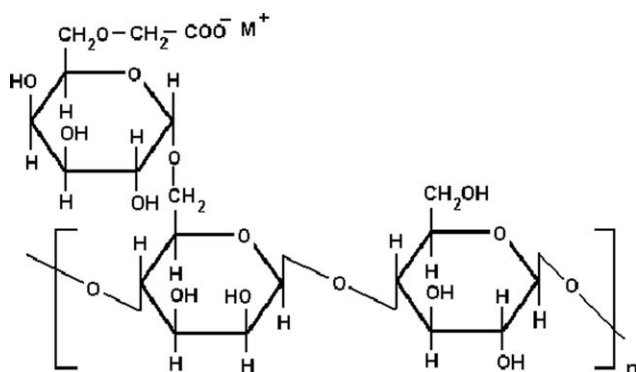


Figure 1 Structure of carboxymethyl guar gum.

other insoluble materials. Before use, CMGG is subjected to soxhlet extraction for about 48 h using 90% ethyl alcohol as suggested by Whitcomb et al.<sup>19</sup> It is then dried in the oven and is used for synthesis.

### Synthesis

The CMGG based graft copolymers are synthesized by solution polymerization technique using ceric-ion-induced redox initiation method. The temperature of the reaction medium is always maintained at  $28 \pm 1^\circ\text{C}$ . As oxygen inhibits the polymerization of vinyl monomer, grafting is carried out in an atmosphere of  $\text{N}_2$ . The detailed synthetic procedure for the series of graft copolymers is given as follows: 1 g of CMGG is dissolved in 100 cc distilled water in a conical flask. The flask is placed in a water bath to maintain the temperature always at  $28 \pm 1^\circ\text{C}$ . Required amount of acrylamide is dissolved in 100 cc distilled water and mixed with CMGG solution. Nitrogen is purged through the reaction mixture for 30 min followed by addition of CAN solution. Nitrogen gas is again purged for 30 min. Then the passing of nitrogen gas supply is stopped and the flask is sealed. The reaction is allowed to continue for 24 h, after which it is terminated by adding saturated solution of hydroquinone. At the end of the reaction, the reaction mixture is precipitated by adding excess quantity of acetone. The product is then dried in a vacuum oven. Subse-

quently, it is pulverized and sieved. In a similar way, three grades of graft copolymers (CMGG-g-PAM 1 to CMGG-g-PAM 3) are synthesized by varying the initiator concentrations. The details of the synthesis parameters are summarized in Table I. The extraction of occluded polyacrylamide is carried out by solvent extraction using a mixture of formamide and acetic acid (1 : 1 by volume).

## CHARACTERIZATION

### Elemental analysis

The elemental analysis of carboxymethyl guar gum and all the graft copolymers (CMGG-g-PAM 1 to CMGG-g-PAM 3) are performed using a Carlo Erba 1108 Elemental Analyzer (Table II). The estimation of only three elements, that is, carbon, hydrogen, and nitrogen is done. The results are shown in this article.

### FTIR analysis

The FTIR spectra of CMGG and the graft copolymer CMGG-g-PAM 2 is recorded in solid state using KBr pellet (Fig. 2). A Thermo Nicolet FTIR Spectrophotometer (Model-Nexus 870 FTIR) is used to record the spectra in the range of  $4000\text{--}400\text{ cm}^{-1}$  wave numbers.

### NMR analysis

The  $^1\text{H}$  NMR analysis of CMGG-g-PAM 2 is performed with JEOL AL300 FTNMR spectrometer (Fig. 3). The spectrum is recorded in the range of 0–7ppm and the solvent used is  $\text{D}_2\text{O}$ .

### Measurement of intrinsic viscosity

Intrinsic viscosity measurement of polymer solutions is carried out with the help of Ubbelohde viscometer (CS/S: 0.00386) at  $25^\circ\text{C}$ . The time of flow is measured for solutions at five different concentrations. From the time of flow of polymer solutions ( $t$ ) and the time of flow of the solvent ( $t_0$ , for distilled water)

TABLE I  
Synthetic Details of the Graft Copolymers of CMGG and Polyacrylamide

Sl. no	Polymer	CMGG (g)	AM (mole)	CAN mole $\times 10^{-5}$	% Conversion	$g_r$	$g_e$	Intrinsic viscosity (dL/g)
I	CMGG-g-PAM 1	1	0.19	12.4	90	12.5	0.95	14.7
II	CMGG-g-PAM 2	1	0.19	9.1	85	12	0.96	15.7
III	CMGG-g-PAM 3	1	0.19	5.4	75	10.5	0.94	15.1

% Conversion =  $[(\text{Wt. of graft copolymer} - \text{Wt. of polysaccharides}) / \text{Wt. of acrylamide monomer}] \times 100$ . Grafting ratio ( $g_r$ ) = weight of pure graft copolymer/weight of polysaccharide. Grafting efficiency ( $g_e$ ) = weight of pure graft copolymer/weight of product mixture. Weight of pure graft copolymer is the weight of the resultant graft copolymer obtained after extraction of polyacrylamide by solvent extraction.

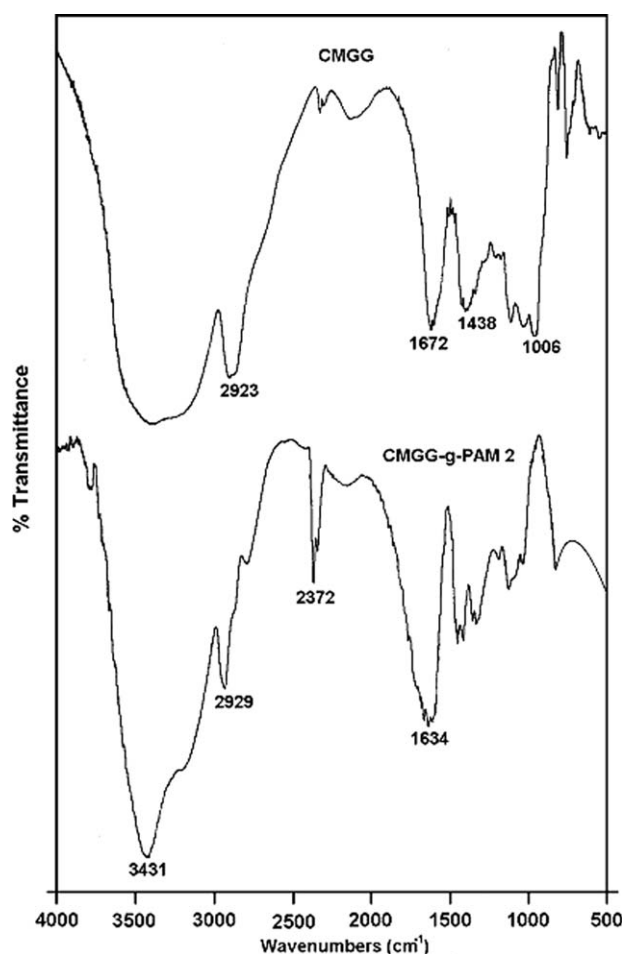
**TABLE II**  
Results of Elemental Analysis of CMGG and Its Graft Copolymers

Polymer	Carbon %	Hydrogen %	Nitrogen %	([−PAM−]/[−AGU−]) <sub>bulk</sub>
CMGG	29.30	4.44	0.12	–
CMGG-g-PAM 1	41.66	7.04	14.77	3.64
CMGG-g-PAM 2	42.60	6.84	15.16	3.62
CMGG-g-PAM 3	42.55	6.79	14.90	3.71

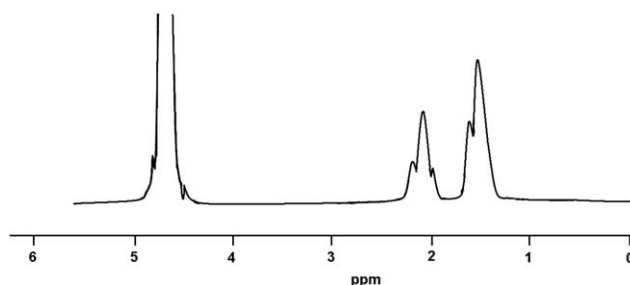
the relative viscosity ( $\eta_{rel} = t/t_0$ ) is obtained. The specific viscosity is calculated from the relation  $\eta_{sp} = \eta_{rel} - 1$ . the reduced viscosity ( $\eta_{sp}/c$ ), and the inherent viscosity ( $\ln \eta_{rel}/c$ ) are then calculated where  $c$  is the polymer concentration in  $\text{g dL}^{-1}$ . The intrinsic viscosity is obtained at the point of intersection after extrapolation of the two plots,  $\eta_{sp}/c$  versus  $c$  and  $(\ln \eta_{rel}/c)$  versus  $c$ , to zero concentration. The intrinsic viscosities of the polysaccharide and all the graft copolymers are reported in Table I.

#### Rheological studies

The rheological measurements of aqueous solutions of CMGG and CMGG-g-PAM 2 are carried out



**Figure 2** FTIR spectra of CMGG, CMGG-g-PAM 2.



**Figure 3** NMR spectrum of CMGG-g-PAM 2.

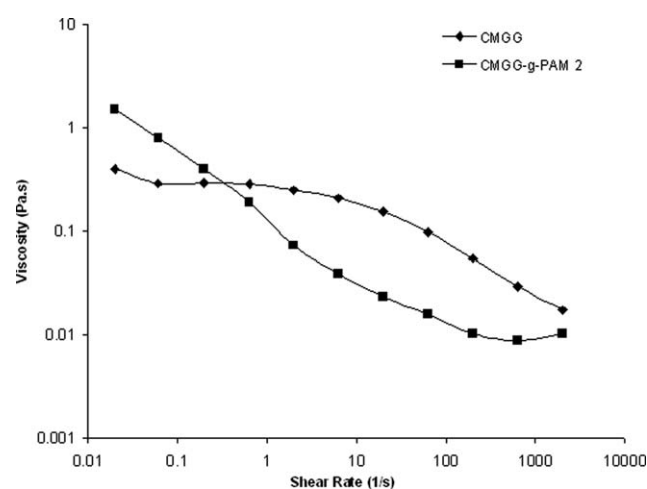
in controlled stress AR-1000 Advanced Rheometer (Fig. 4). For these measurements, a 2° cone of diameter 4 cm and with truncation 46  $\mu\text{m}$  is used. The temperature of the system is maintained at 30°C throughout the experiment.

#### Scanning electron microscopy

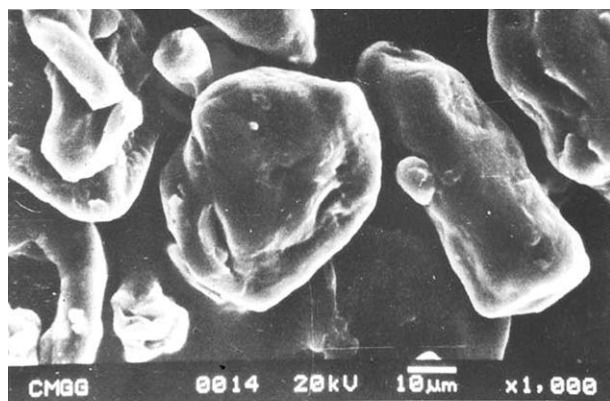
For SEM study of the polymer samples, CAM SCAN SERIES-2 (Cambridge Scanning Company, UK) is used. For this study CMGG is used in the powder form, whereas the graft copolymer CMGG-g-PAM 2 is studied in small granular form. Figure 5(a,b) show the SEM of CMGG and CMGG-g-PAM 2, respectively.

#### SLS analysis for determination of weight average molecular weight

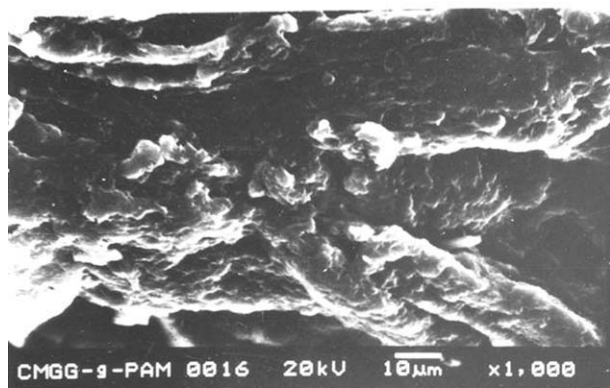
The weight average molecular weight ( $M_w$ ) of CMGG and CMGG-g-PAM 2 are determined by DLS-7000 Super Dynamic Light Scattering Spectrophotometer.  $\text{Ar}^+$  ( $\lambda = 488 \text{ nm}$ ) laser is used for study with toluene as the reference liquid<sup>20</sup> (Table III). Five highly diluted concentrations of graft copolymer solutions in water as solvent are



**Figure 4** Viscosity versus shear rate curves of CMGG and CMGG-g-PAM 2.



(a)



(b)

**Figure 5** Scanning Electron Micrographs of (a) CMGG and (b) CMGG-g-PAM 2.

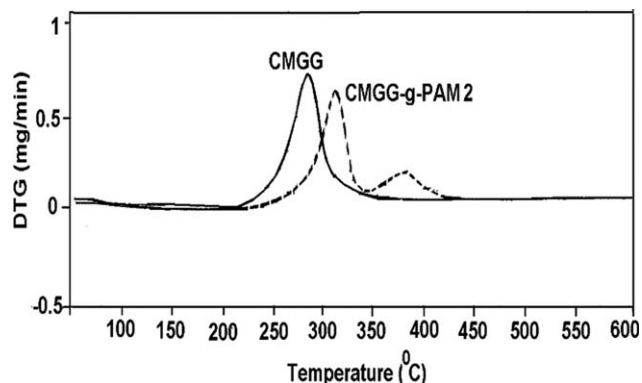
prepared and the  $dn/dc$  value is determined using refractometer. The  $dn/dc$  value is observed to be 0.1394. Further the scattering intensities of water and various concentrations of graft copolymer solutions were measured and the molecular weight was determined by Zimm plot.

### Thermogravimetric analysis

The thermal analysis of CMGG and CMGG-g-PAM 2 are carried out with a Perkin-Elmer, PYRIS Diamond TG/DTA (USA) (Fig. 6). The analysis of the samples is performed up to a temperature of 450°C, starting from room temperature in an atmosphere of nitrogen. The heating rate is uniform in all cases at 10°/min.

**TABLE III**  
Results of SLS Analysis

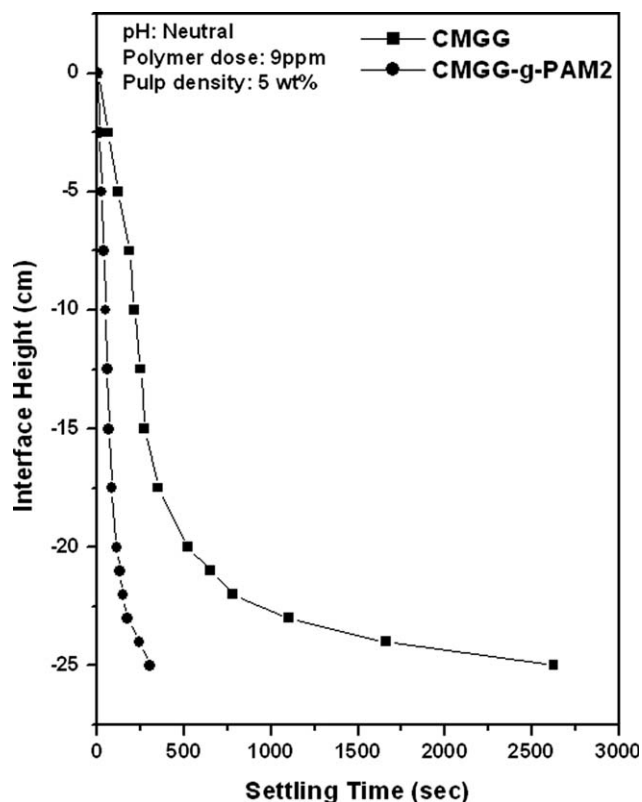
Polymers	Molecular weight ( $M_w$ ) (g/mol)
CMGG	$1.22 \times 10^4$
CMGG-g-PAM 2	$4.78 \times 10^6$



**Figure 6** DTG curves of CMGG and CMGG-g-PAM 2.

### Flocculation study

The test employs a 100-mL stoppered graduated cylinder and stopwatch. The slurry sample is placed in the cylinder, the polymer sample is added, and the cylinder is inverted 10 times. After mixing, the cylinder is set upright and the height of the interface between the supernatant liquid and setting solid bed is measured over time. The settling test is carried out using kaolin suspension. Comparison of settling efficiency of CMGG-g-PAM 2 is done with CMGG in Figure 7.



**Figure 7** Settling curves of CMGG and CMGG-g-PAM 2 in kaolin suspension.

## RESULTS AND DISCUSSION

### Synthesis

The synthetic details of the graft copolymerisation reaction based on polysaccharides and PAM are given in Table I. The amount of CAN is varied keeping the concentration of CMGG and acrylamide constant.

Grafting is undertaken by ceric ion induced redox polymerization technique. The mechanism of ceric ion initiation involves the formation of chelate complex that decomposes to generate free radical sites on the polysaccharide backbone. These active free radical sites in the presence of acrylic monomers generate graft copolymers. The average number of grafting sites per backbone molecule depends on the ratio of concentration of ceric ion to polysaccharides. Following a simplistic approach, a low concentration of catalyst should initiate a few grafting sites resulting in longer polyacrylamide chains as against a high concentration of catalyst that will initiate a larger number of grafting sites thus making the average polyacrylamide chains shorter for the same acrylamide concentration. Considering the intrinsic viscosity values, the graft copolymer having fewer and longer PAM branches exhibits higher intrinsic viscosity than the graft copolymer having larger and shorter PAM chains. This is reflected in the graft copolymers in the series.

### Elemental analysis

The results of elemental analysis of CMGG and its graft copolymers are given in Table II. The polysaccharides CMGG does not show any significant presence of nitrogen. However, the negligible amount of nitrogen may be due to the trace quantities of unisolated proteins in the polysaccharides. It has been found that there is a considerable percentage of nitrogen in the graft copolymers, which is accounted for the presence of grafted PAM chains. In the series of graft copolymers based on CMGG, the variation in the nitrogen content, although not much, is significant in case of CMGG-g-PAM 2. The higher percentage of nitrogen is due to the increased PAM content in the graft copolymer.

The bulk graft concentration of the copolymers can be derived from the Carbon to Nitrogen ratio obtained from elemental analysis. The graft concentration in terms of number of polyacrylamide (PAM) repeat units per anhydroglucose (AGU) repeat unit, or the  $([-\text{PAM-}]/[-\text{AGU-}])_{\text{bulk}}$  molar ratio, can be obtained readily from the  $([\text{C}]/[\text{N}])_{\text{bulk}}$  molar ratio by taking into account the carbon stoichiometries of the graft and main chains, and the carbon to nitrogen ratio of the graft copolymer. Thus the  $([-\text{PAM-}]/[-\text{AGU-}])_{\text{bulk}}$  molar ratio can be calculated from the following relationship.

$$([-\text{PAM-}]/[-\text{AGU-}])_{\text{bulk}} = 6/3([\text{C}] - [\text{N}])_{\text{bulk}}/[\text{N}]_{\text{bulk}}$$

where the factors 6/3 accounts for the fact that there are six and three carbon atoms per repeat unit of graft copolymer and polyacrylamide respectively. The elemental analysis results suggest that the bulk graft concentration is lowest in case of CMGG-g-PAM 2 having optimum nitrogen content.

### FTIR analysis

The grafting of copolymer is confirmed by FTIR spectroscopy. The FTIR spectra of CMGG and CMGG-g-PAM 2 are shown in Figure 2.

In the FTIR spectrum of CMGG the peaks present at  $1672\text{ cm}^{-1}$  and  $1438\text{ cm}^{-1}$  represent the presence of asymmetric and symmetric stretching of  $\text{COO}^-$  group. The broad peak at  $3600\text{ cm}^{-1}$  is due to O—H stretching band.

In the FTIR spectrum of CMGG-g-PAM 2, O—H stretching band of hydroxyl group of CMGG and N—H stretching band of amide group of PAM overlap with each other and lead to a broad band appearing at  $3431\text{ cm}^{-1}$ . A broad band around  $1650\text{ cm}^{-1}$  is obtained due to amide-I (CO stretching), amide-II (NH bending) band, and asymmetric stretching of  $\text{COO}^-$  groups. C—N and C—H stretching bands appear at  $1402$  and  $2929\text{ cm}^{-1}$ , respectively.

### NMR analysis

The grafting of copolymer is confirmed by NMR spectroscopy. In Figure 3, the resonances at 2.1 and 1.5 ppm are attributed to the protons of -CH and  $\text{CH}_2$  groups respectively, of amide in the PAM molecule. The results prove that PAM is found in the product. The ethylenic protons peaks are absent showing the removal of monomer in the graft copolymer.

### Intrinsic viscosity measurement

Keeping other factors constant, for two polymers of approximately similar molecular weight, a branched polymer will have lower hydrodynamic volume and hence a lower intrinsic viscosity as compared to its linear counterpart. Further, along a series of branched polymers, the longer the branches, the higher will be the intrinsic viscosity and vice versa. This has been observed in practice.

In case of CMGG graft copolymers considering the series of three graft copolymers (CMGG-g-PAM 1 to CMGG-g-PAM 3), maximum chain length is obtained at optimum CAN concentration in the graft copolymer CMGG-g-PAM 2 showing highest intrinsic viscosity. The intrinsic viscosity values of all graft copolymers of CMGG and acrylamide are given in Table I.

### Rheological studies

The rheological studies of aqueous solution of CMGG and CMGG-g-PAM 2 are carried out at 2 wt %. Plots of viscosity versus shear rate are plotted in two axes in logarithmic scales.

Figure 4 shows the relationship between viscosity and shear rate  $\gamma$ . Both the aqueous solutions of CMGG and CMGG-g-PAM 2 show non-Newtonian behavior. The viscosity of the polymer solutions decreases with increase in shear rate. It is observed that at lower shear rates CMGG-g-PAM 2 solution has higher viscosity but with increase in shear rate its viscosity decreases than the polysaccharide CMGG solution. In case of CMGG solution, the solvent can attach through association with ionic groups of the polymer thus the decrease in viscosity is less compared to its graft copolymer at higher shear rates.

### Scanning electron microscopy

Figure 5(a,b) shows the scanning electron micrographs of CMGG and CMGG-g-PAM 2. Surface morphology of CMGG before grafting shows a granular structure, which has been changed to fibrillar form after grafting. Thus, comparison of these figures reveals the changes due to grafting.

### SLS analysis

From Table III it is evident that the molecular weight of graft copolymer is more than the original polysaccharide. The high molecular weight polyacrylamide branches grafted on the polysaccharide backbone leads to high molecular weight graft copolymer.

### Thermogravimetric analysis

The DTG curves of CMGG and CMGG-g-PAM 2 in nitrogen atmosphere are shown in Figure 6. In case of CMGG weight loss is observed at 275°C when the polymer decomposition takes place. In case of CMGG-g-PAM 2, the degradation of the polymer takes place in two stages. The first degradation at 325°C is for decomposition CMGG backbone. The second degradation at 380°C is due to the degradation of PAM chain. From the DTG curves, it is obvious that CMGG-g-PAM 2 is thermally more stable as compared with CMGG. So, from the DTG results, we conclude that the grafting of PAM chains onto the polysaccharide backbone enhances the thermal stability of the polysaccharides.

### Flocculation study

Figure 7 is a comparison of settling efficiency of CMGG and CMGG-g-PAM 2 in kaolin suspension. It is observed that the graft copolymer shows better flocculation efficiency than the original polysaccharide. The

dangling longer branches of polyacrylamide onto rigid polysaccharide backbone, helps in better approachability towards the contaminants in case of graft copolymer thus leading to its better flocculation efficiency.

### CONCLUSIONS

The present results conclude the occurrence of grafting PAM onto CMGG. Variation in the CAN concentration results in a series of graft copolymers with varying number and length of PAM chains evident from different intrinsic viscosities. Study of FTIR spectra provides a strong proof of grafting. Rheology study reveals that the decrease in viscosity is less in case of CMGG compared to its graft copolymer at higher shear rates. The difference in morphological features between CMGG and its graft copolymer as evident from SEM indicates grafting. DTG results exhibit different thermal decomposition patterns for CMGG and its graft copolymer and it is observed that the graft copolymer is thermally more stable. From the flocculation study it can be concluded that grafting leads to enhanced flocculation performance.

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