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Graft [partially carboxymethylated guar gum-g-poly *N*-(hydroxymethyl) acrylamide] copolymer: From synthesis to applications

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ABSTRACT

Graft copolymer of *N*-(hydroxymethyl) acrylamide with carboxymethylated guar gum was synthesized and the reaction conditions were optimized for better yield using potassium peroxymonosulfate and thiourea as a redox initiator. The optimum reaction conditions for grafting have also been determined by studying the effect of *N*-(hydroxymethyl) acrylamide, hydrogen ion, peroxymonosulphate, thiourea concentration and carboxymethylated guar gum along with time and temperature. Experimental results show that maximum grafting has been obtained at 1.4 g dm^{-3} concentration of carboxymethylated guar gum and 16×10^{-2} mol dm^{-3} concentration of *N*-(hydroxymethyl) acrylamide. It has been observed that grafting ratio, add on, conversion, efficiency and rate of grafting increase up to 6.0×10^{-3} mol dm^{-3} of hydrogen ion, 2.4×10^{-3} mol dm^{-3} of thiourea, 14×10^{-3} mol dm^{-3} of peroxymonosulphate and 35 °C of temperature. Grafted copolymer has been characterized by FTIR spectroscopy and thermogravimetric analysis. Water swelling, flocculating, and metal ion uptake properties of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide have been determined.

1. Introduction

Naturally occurring carbohydrate polymers are found in the plant, animal and microbial kingdoms. In recent years, much attention has been paid on chemical modification of natural macromolecules (Kumar, Srivastava, & Behari, 2009; Mishra, Tripathy, Yadav, Sand, & Behari, 2010; Tripathy, Mishra, Yadav, Sand, & Behari, 2009). To increase the paramount contributions toward their industrial applications, this study has been performed, which is concerned with the synthesis of a new type of graft copolymer [partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide]. Partially carboxymethylated guar gum [CmgOH; degree of substitution (DS) = 0.291] has been chosen as backbone (Thaker & Trivedi, 2005) which is derivative of naturally occurring guar gum and constituted of galactomannan polysaccharide isolated from the seed endosperm and having linear chain β-D-mannopyranose joined by (1–4) linking with α-D-galactopyranosyl units (Sinha & Kumria, 2001) attached by 1, 6 links in ratio of 1:2. Because of the immense potential and low price, this versatile polymer is used as a vehicle for oral controlled release purpose (Guo, Skinner, Harcum, & Barnum, 1998). Guar gum and its derivatives find numerous other applications, such as in oil industry. They also act as major ingredients in drilling muds and fingering fluids whereas in textile industry help to improve printing quality (Turk & Schneider, 2000). Even though guar gum and its derivatives enjoy wide range of applications, however, like other polysaccharides this suffer from the drawback like easier susceptibility of microbial attack. The grafting provides an efficient route not only removing the drawback but also improving its properties toward swelling and flocculation. Up to date many investigations have been carried out in view of preparing biopolymer based advanced materials, but reports on grafting onto the partially carboxymethylated guar gum are scantily available. *N*-(Hydroxymethyl) acrylamide (HMA) is one of the hydrophilic monomers. It is reported that the lower critical solution temperature of thermosensitive hydrogel may rise close to physiologic temperature by introducing a proportion of HMA (Chen, Liu, Liu, & Ma, 2009; Wei et al., 2008). Moreover, HMA can bind with some dyes, for example, an affinity dye Cibacron Blue F3GA, which contains Cl. Therefore, ligands having interaction abilities with biological molecules may be incorporated more easily into the hydrogel network (Yildiz, Iik, & Ki, 2001). Therefore, present work aimed to prepare graft copolymer of partially carboxymethylated guar gum and *N*-(hydroxymethyl) acrylamide so that to develop a product with high water swelling capacity and could

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be exploited industrially for metal ion sorption and flocculation. Synthesis of carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide has been done using peroxymonosulphate/thiourea redox pair under nitrogen atmosphere.

2. Experimental

2.1. Materials

N-(hydroxymethyl) acrylamide (HMA) (Aldrich) has been purified by removing the inhibitor by partition method employing diethyl ether as a solvent. Carboxymethylated guar gum (CMG) was obtained as gift sample from Hindustan Gum Ltd. India. Potassium peroxymonosulphate (Sigma) and Thiourea (E. Merck) were used as such. For maintaining hydrogen ion concentration sulphuric acid (E. Merck) is used and all the solutions were prepared in triple distilled water. The other chemicals used were of analytical grade and used as such without further purification. For the flocculation, coking and non coking coals were received from steel plant Bokaro, India.

2.2. Procedure for graft copolymerization

For each experiment partially carboxymethylated guar gum solution has been prepared by addition of weighed amount of partially carboxymethylated guar gum (0.6–1.4 g dm^{-3}) into reactor containing triple distilled water with rapid stirring in reactor. The calculated amount of *N*-(hydroxymethyl) acrylamide (8.0–24.0 $\times 10^{-2}$ mol dm^{-3}), potassium peroxymonosulphate (0.6–1.4 $\times 10^{-2}$ mol dm^{-3}), thiourea (0.8–4.0 $\times 10^{-3}$ mol dm^{-3}), sulphuric acid (0.2–1.0 $\times 10^{-2}$ mol dm^{-3}) has been added to the reactor at constant temperature and a slow stream of pure nitrogen is passed. After 30 min, a known amount of deoxygenated potassium peroxymonosulphate, solution is added to initiate the reaction. The experiments were performed under pure nitrogen gas. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring it in to water/methanol mixture (ratio 1:5). The grafted sample has been separated by filtration and then dried and weighed.

2.3. Separation of homopolymer

The filtrate has been concentrated by distillation under reduced pressure in the presence of little of amount hydroquinone. The poly *N*-(hydroxymethyl) acrylamide was precipitated by pouring concentrated filtrate into pure methanol. The poly *N*-hydroxymethyl acrylamide thus obtained, has been separated, dried and weighed.

2.4. Characterization of graft copolymer

The graft copolymer has been characterized as reported in our previous publication (Pandey, Verma, Yadav, & Behari, 2014)

2.5. Study of properties

2.5.1. Swelling

For swelling study, different samples of graft copolymer have been synthesized at different concentrations of *N*-(hydroxymethyl) acrylamide from 8 $\times 10^{-2}$ to 24 $\times 10^{-2}$ mol dm^{-3}. The preweighed samples (0.02 g) of each were immersed in 20 ml of triple distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen samples were then removed from triple distilled water, quickly wiped with filter paper to remove droplets on the surface and weighed. The percent swelling (P_s) and swelling ratio (S_r) have been calculated by using following expressions (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000)

$$S_r = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}} \quad (1)$$

$$P_s = S_r \times 100 \quad (2)$$

2.5.2. Metal ion sorption test

The metal ion sorption studies of graft copolymer have been performed as reported in previous publication (Yadav, Mishra, Sand, & Behari, 2011).

2.5.3. Flocculation

In 1.0 l beaker, 200 cc of 1% wt. coal suspension (in water) was taken. The beaker was placed on flocculator dipping the stirrer blade in the suspension. Under a low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for half an hour. Clean supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (DIGITAL NEPHELOMETER MODEL 341 (EI) supplied by ISO-TECH SYSTEM) to express the turbidity in nephelometric unit (N.T.U.).

2.6. Characterization of graft copolymer partially carboxymethylated guar gum-g-N-(hydroxymethyl) acrylamide

2.6.1. IR spectroscopy

The IR spectra of pure partially carboxymethylated guar gum and grafted samples have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1}.

2.6.2. Thermogravimetric analysis

The thermograms have been recorded on NETZSCH – STA 409C/CD thermal analyzer from 0 °C to 1400 °C temperature range and with a heating rate of 15 °C/min in nitrogen atmosphere.

3. Results and discussions

3.1. Determination of optimum grafting conditions

The optimum reaction conditions for maximum percentage of grafting of *N*-(hydroxymethyl) acrylamide onto partially carboxymethylated guar gum by using potassium peroxymonosulphate (PMS)/thiourea redox system in the presence of hydrogen ion (H^+) have determined.

3.1.1. Effect of concentration of N-(hydroxymethyl) acrylamide

The effect of concentration of *N*-(hydroxymethyl) acrylamide on grafting parameters has been investigated by varying the concentration of *N*-(hydroxymethyl) acrylamide (HMA) from 8.0 $\times 10^{-2}$ to 24.0 $\times 10^{-2}$ mol dm^{-3}. It has been observed that grafting ratio, add on, efficiency and rate of grafting increase on increasing the concentration up to 16.0 $\times 10^{-2}$ mol dm^{-3} and thereafter, grafting parameters decrease (Fig. 1a). However the formation of homopolymer shows a reverse trend with respect to grafting efficiency. This behavior is attributed to accumulation of monomer molecules at close proximity of polymeric backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of carboxymethylated macro radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules leading lowering of termination. But on further increasing the concentration of *N*-(hydroxymethyl) acrylamide, the grafting parameters decrease due to formation of more homopolymer.

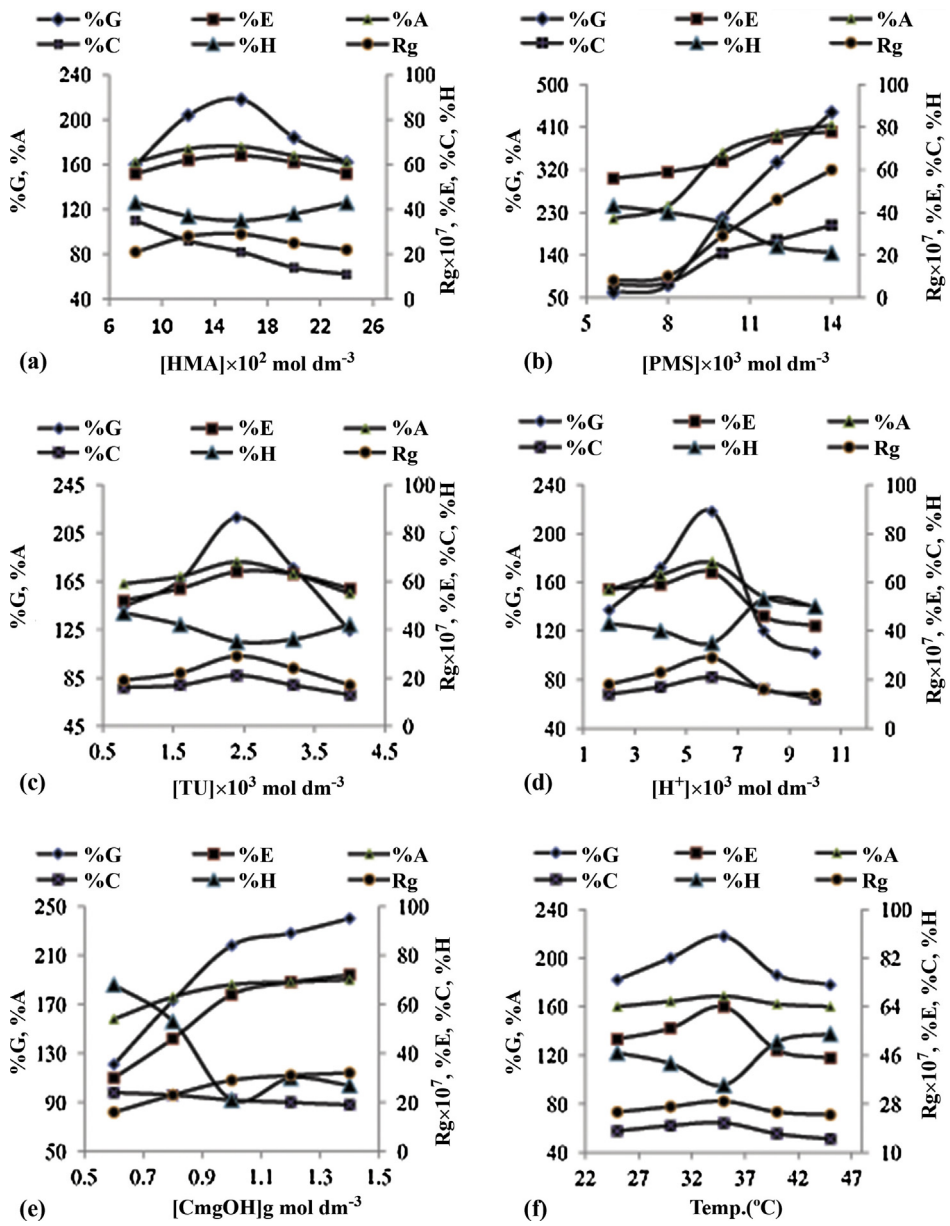


Fig. 1. (a) Effect of *N*-(hydroxymethyl) acrylamide concentration. (b) Effect of peroxymonosulphate concentration. (c) Effect of thiourea concentration. (d) Effect of sulphuric acid concentration. (e) Effect of partially carboxymethylated guar gum concentration. (f) Effect of temperature.

3.1.2. Effect of concentration of peroxymonosulphate

The effect of peroxymonosulphate ion concentration on grafting reaction has been studied and the results were summarized in Fig. 1b. It was observed that grafting ratio, efficiency, add on conversion and rate of grafting were increased on increasing throughout the cited range i.e. from 6.0×10^{-3} to 14.0×10^{-3} mol dm^{-3}. This behavior might be attributed due to progressive reduction of PMS by thiourea producing primary free radicals, which attack the carboxymethylated guar gum molecules creating more active sites, to which monomer addition takes place.

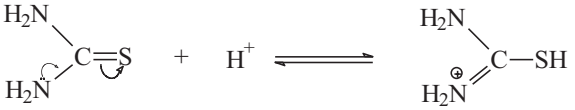
3.1.3. Effect of concentration of thiourea

The variation of thiourea concentration (TU) from 0.8×10^{-3} to 4.0×10^{-3} mol dm^{-3} reveals that of grafting ratio, add on, conversion, efficiency and rate of grafting increase on increasing the thiourea concentration up to 2.4×10^{-3} mol dm^{-3} due to availability of more primary free radicals ($R^{\bullet} = R_1S^{\bullet}$ and $SO_4^{\bullet -}$), which might be formed due to reduction of peroxymonosulphate by thiourea. However, on further increasing the concentration of thiourea from 2.4×10^{-3} to 4.0×10^{-3} mol dm^{-3}, the decrement in grafting parameters has been found which is probably due to premature termination of *N*-(hydroxymethyl) acrylamide (HMA) radicals giving rise to formation of more homopolymer. The results are represented by Fig. 1c.

3.1.4. Effect of concentration of hydrogen ion

The concentration of hydrogen ion plays an important role during the reaction. The effect of hydrogen ion concentration has been studied by varying the concentration from 2.0×10^{-3} mol dm^{-3} to 10.0×10^{-3} mol dm^{-3}. It has been observed that grafting ratio, add on, conversion, efficiency and rate of grafting increase due to protonation of thiourea (Tripathy et al., 2009b), on increasing the hydrogen ion concentration up to 6.0×10^{-3} mol dm^{-3}, which in

turn, protonated species react with peroxymonosulphate to give more primary free radicals (Fig. 1d).



Thiourea (R_1S) **Isothiourea (R_1SH)**

But on further increasing the concentration of $[H^+]$ ions beyond 6.0×10^{-3} mol dm^{-3}, the grafting parameters decrease while homopolymer increases. It could be explained by following reasons

(1) It is due to premature termination of *N*-(hydroxymethyl) acrylamide radicals giving rise to the formation of homopolymer.
(2) On increasing the hydrogen ion concentration, formation of inactive species (H_2SO_5) increases due to which concentration of HSO_5^- decreases resulting in production of less free radical, thereby decreasing the grafting parameters.

$$HSO_5^- + H^+ \rightarrow H_2SO_5$$

3.1.5. Effect of concentration of partially carboxymethylated guar gum

The effect of concentration of partially carboxymethylated guar gum has been observed with an aim to study the effect of its concentration (from 0.6 to 1.4 g dm^{-3}) on grafting parameters. The grafting parameters increase continuously on increasing the concentration of partially carboxymethylated guar gum (Fig. 1e). This may be due to greater availability of grafting site at partially carboxymethylated guar gum.

3.1.6. Effect of temperature

The results, for grafting parameters at different temperatures between 25 °C and 45 °C, are summarized in Fig. 1f. The grafting parameters increase up to 35 °C and thereafter decrease to some extent with increase in temperature. The increment in grafting parameters from 25 °C up to 35 °C is attributed due to the increase in the formation of active sites on account of enhanced production of primary free radicals with increase in temperature.

The decrement in grafting parameters from the temperature 35 °C to 45 °C could be explained as follows.

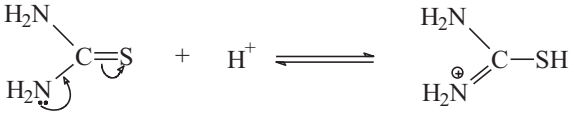
(1) It may be due to the premature termination of growing grafted chains by excess free radicals at higher temperature.
(2) Beyond the optimum value increase in temperature may lead to the decomposition of peroxymonosulphate into HSO_4^-, H_2O, O_2. Since O_2 acts as a scavenger for free radicals, which reacts with primary free radicals thereby lowering the free radical concentration.

3.1.7. Effect of time

To investigate the effect of time on graft copolymerization, the reaction has been carried out by varying the duration of time from 60 to 180 min. It has been found that grafting ratio (%*G* = 136–218), add on (%*A* = 57.6–68.5), conversion (%*C* = 17–21), efficiency (%*E* = from 49.3 to 64.0) and rate of grafting increase in beginning from 60 to 120 min and thereafter these parameters decrease (%*G* = 218–140, %*A* = 68.5–58.3, %*E* = 64.0–47, %*C* = 21.0–18.4). This is attributed due to propagation of grafting chains which takes place due to availability of more active species, which accounts for higher grafting. On further increasing the time interval, beyond 120 min, all the active sites get exhausted as the mutual annihilation of growing grafted chains occur, so that grafting parameters decrease.

3.2. Mechanism

A tentative mechanism has been proposed on the basis of results obtained. Initially thiourea reacts with hydrogen ion to give protonated species which react with peroxymonosulphate to form a complex. The complex dissociates to give primary free radicals $R_1S^\bullet$ and $SO_4-^\bullet$ represented by $R_1^\bullet$. These radicals abstract hydrogen atom from the partially carboxymethylated guar gum (CmgOH) molecules, producing macroradicals of partially carboxymethylated guar gum. The monomer molecules, which are in close vicinity of the reaction sites, become acceptors of carboxymethyl guar gum radicals resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules. In this way grafted chains grow and terminate by coupling to give graft copolymer. The probable reaction mechanism can be represented as



Thiourea (R_1S) **Isothiourea (R_1SH)**

$$R_1SH + HSO_5^- \rightleftharpoons \text{Complex}$$

$$\text{Complex} \Rightarrow R_1S^\bullet + H_2O + SO_4^{\bullet -}$$

Initiation

$$CmgOH + R^\bullet \rightarrow CmgO^\bullet + RH$$

$$M + R^\bullet \rightarrow RM^\bullet$$

[where $R^\bullet = R_1S^\bullet$ or $SO_4^{-\bullet}$, CmgOH = partially carboxymethylated guar gum and M = Monomer].

Propagation

$$CmgO^\bullet + M \longrightarrow CmgOM_1^\bullet$$

$$CmgOM_1^\bullet + M \longrightarrow CmgOM_2^\bullet$$

$$CmgOM_2^\bullet + M \longrightarrow CmgOM_3^\bullet$$

.....

.....

$$CmgOM_{n-1}^\bullet + M \longrightarrow CmgOM_n^\bullet$$

$$RM_1^\bullet + M \longrightarrow RM_2^\bullet$$

$$RM_2^\bullet + M \longrightarrow RM_3^\bullet$$

.....

.....

$$RM_{n-1}^\bullet + M \longrightarrow RM_n^\bullet$$

Termination

$$CmgOM_n^\bullet + CmgOM_m^\bullet \rightarrow \text{Graft copolymer}$$

$$CmgOM_n^\bullet + RM_n^\bullet \rightarrow \text{Graft copolymer}$$

$$RM_n^\bullet + RM_m^\bullet \rightarrow \text{Homopolymer}$$

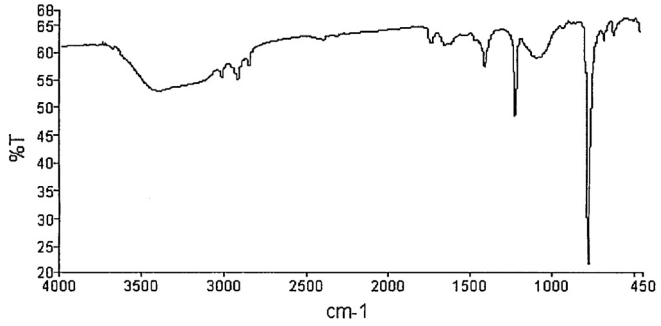


Fig. 2. IR spectrum of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide.

3.3. Evidence of grafting

3.3.1. IR spectroscopy

The infra red spectra analysis has been utilized to prove grafting, for these IR spectra of partially carboxymethylated guar gum (Yadav, Sand, Mishra, & Behari, 2010) and partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide, have been recorded in the range of 500–4000 cm^{-1}. On comparing the IR spectra of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide (Fig. 2), a band at 3450.0 cm^{-1} is due to OH stretching vibration in the spectrum of partially carboxymethylated guar gum shifting to 3401.1 cm^{-1} in partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide, indicates the participation of hydroxyl groups in grafting process. The grafting is further confirmed by characteristic absorption bands at 1627 cm^{-1} and 1404.45 cm^{-1} due to ⟩C═O stretching vibration and C—N stretching vibration of secondary amide of monomer respectively. The appearance of additional peaks in spectrum of graft copolymer and shifting of OH stretching vibration appeared in the spectrum of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide from partially carboxymethylated guar gum showed that grafting might have taken place on OH sites of partially carboxymethylated guar gum molecules.

3.3.2. Thermogravimetric analysis

Thermogravimetric curve of partially carboxymethylated guar gum (Fig. 3) shows single step degradation. The weight loss 1.5% is due to loss absorbed water at approximately 95 °C. The polymer decomposition temperature has been found at approximately 75 °C. The weight loss increases with increase in temperature from 75 °C to 184 °C and thereafter decreases and attains maximum at approximately 284 °C. The integral procedural decomposition temperature which accounts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve. Thus thermal stability of carboxymethylated guar gum and its graft copolymers has also been determined by calculating IPDT values. The integral procedure decomposition temperature (IPDT) proposed by Doyle (Doyle, 1961) has been correlated the volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials (Vyazovkin & Sbirrazzuoli, 2006). IPDT was calculated from

$$\text{IPDT}\,(^{\circ}\text{C}) = A * K * (T_f - T_i) + T_i \quad (3)$$

$$A^* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (4)$$

$$K^* = \frac{S_1 + S_2}{S_1} \quad (5)$$

Table 1
Swelling capacity of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide.[a]

Sample code	[HMA] × 10^2 mol dm^{-3}	%*G*	P_s	S_r
A	8	160.0	105.3	1.05
B	12	204.0	120.7	1.20
C	16	218.0	150.4	1.50
D	20	184.0	130.0	1.30
E	24	162.0	127.8	1.27

A, B, C, D, E indicates the sample of graft copolymer [partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide].

[a] Swelling capacity of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide [CmgOH] = 1.0 g dm^{-3}, [PMS] = 1.0 × 10^{-2} mol dm^{-3}, [TU] = 2.4 × 10^{-3} mol dm^{-3}, [H^+] = 6 × 10^{-3} mol dm^{-3}, Temp. = 35 °C, Time = 120 min.

where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, T_i the initial experimental temperature, T_f the final experimental temperature. S_1, S_2 and S_3 values for calculating A^* and K^* are taken from our previous work (Yadav, Sand, & Behari, 2012). The integral procedural decomposition temperature (IPDT) is 189 °C. T_{max}, the temperature at which maximum degradation occurred, is 268 °C and final decomposition temperature (FDT) has been observed at approximately 900 °C. But in case of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide, the weight loss 1.4% at approximately 55 °C might be due to loss of absorbed water. The polymer decomposition temperature (PDT) was found at approximately 77 °C. Carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide shows single step degradations (Fig. 4). It has been found that degradation of carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide starts at approximately 100 °C temperature. The rate of weight loss increases with increase in temperature from 110 °C to 184.7 °C and there after decreases and attains maximum at approximately 326 °C. T_{max}, the temperature at which maximum degradation occurred, is 278 °C. The integral procedural decomposition (IPDT) and final decomposition temperature (FDT) have been found at 1792 °C and 500 °C respectively. On comparing the thermograms of parent backbone (carboxymethylated guar gum) and graft copolymer [carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide], it has been observed that final and integral procedural decomposition temperature have been found to be higher for graft copolymer. This indicates that graft copolymer is thermally stable than backbone.

3.4. Study of the properties

3.4.1. Swelling test

An increase in the weight of graft copolymer has been recorded by performing swelling test. The results have been summarized in Table 1, which indicates that swelling ratio and swelling percent depend on the concentration of monomer used while grafting. As HMA is a hydrophilic monomer, it increases the water retention character of graft copolymer. On increasing the concentration of HMA, grafting is increased, which may result into coiling network of poly(HMA), thus imbibes more water. Both factors, the presence of carboxymethyl group of substrate and a hydrophilic monomer, are responsible for good swelling capacity of graft copolymer. Swelling percent is increased with increased percent grafting, because on increasing HMA concentration pendant chain of poly(HMA) grows thereby increasing the swelling capacity of graft copolymer.

3.4.2. Metal ion sorption behavior of partially carboxymethylated guar gum and its graft copolymer

The results of sorption behavior of partially carboxymethylated guar gum and its grafted polymer with *N*-(hydroxymethyl) acrylamide have been determined in terms of percent ion uptake (P_u),

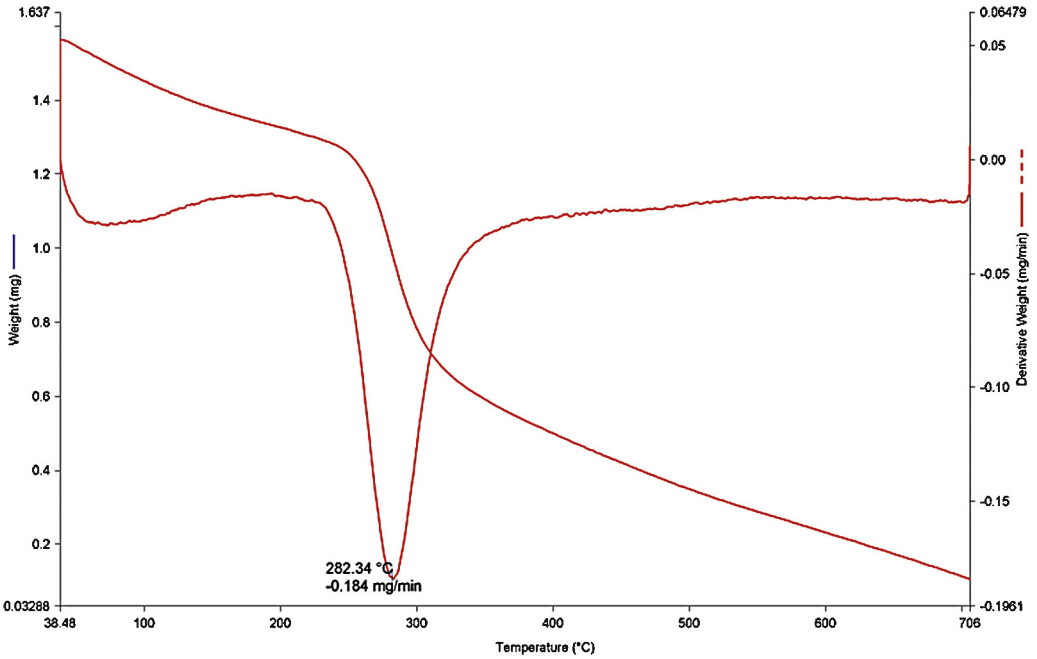


Fig. 3. Thermogravimetric trace of partially carboxymethylated guar gum.

partition coefficient (K_d), retention capacity (Q_r). The results are given in Table 2. It has been observed that the values of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly as percent grafting increases, which might be due to the fact that as grafting increases, the sorption sites for metal ions are increased due to availability of additional functional groups of monomer grafted i.e. *N*-(hydroxymethyl) acrylamide and increment in sorption capacity takes place due to the incorporation of its pendant chain of poly [*N*-(hydroxymethyl) acrylamide], so greater the grafting, greater will be the sorption of metal ion. Results also show that Pb^{2+} was least uptakable in comparison to Zn^{2+} and Ni^{2+} metal ions, which have been used.

3.4.3. Flocculation properties

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone partially carboxymethylated guar gum and graft copolymer of *N*-(hydroxymethyl) acrylamide with partially carboxymethylated guar gum. Plots of supernatant turbidity versus polymer dosage for coking and noncoking coals are presented in Fig. 5. It is obvious that grafted copolymer [partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide] shows better performance with low turbidity than partially carboxymethylated guar gum itself. In grafted copolymer,

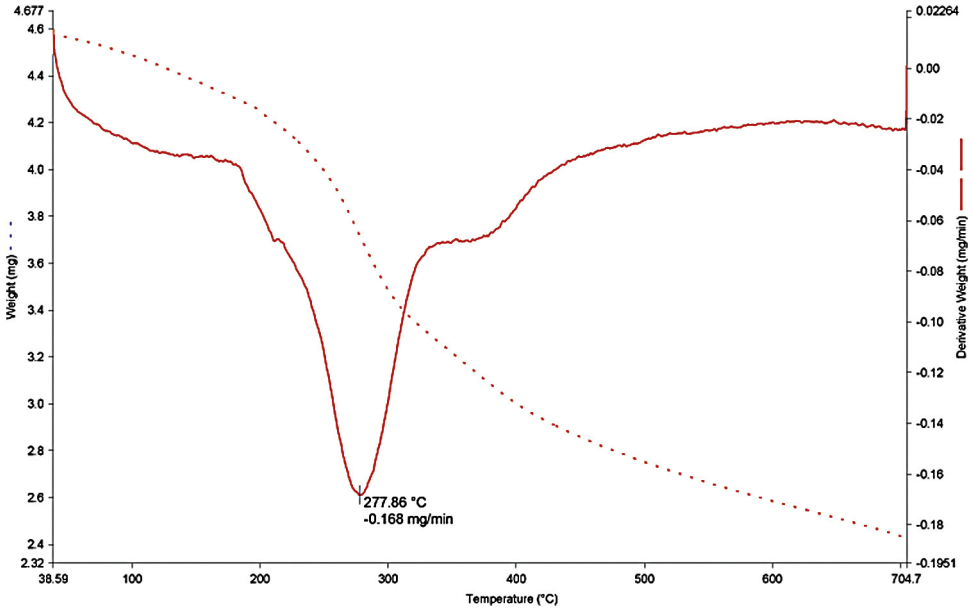


Fig. 4. Thermogravimetric trace of partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide.

Table 2
Metal ion sorption.[a]

Sample[b]	CmgOH	A	B	C	D	E
[HMA] × 102 mol dm^{-3}	–	8.0	12.0	16.0	20.0	24.0
% Grafting	–	160	204	218	184	162
Percent uptake (P_u)						
Pb^{2+}	1.2	1.4	3.4	4.5	4.2	3.4
Ni^{2+}	2.8	2.9	5.8	7.0	6.4	5.1
Zn^{2+}	2.1	2.3	4.9	5.8	5.3	4.4
Partition coefficient (K_d)						
Pb^{2+}	7.3	8.1	18.9	26.1	25.2	24.1
Ni^{2+}	13.5	16.5	31.8	42.2	39.5	38.3
Zn^{2+}	10.4	12.5	24.0	33.3	31.7	30.0
Retention capacity (Q_r)						
Pb^{2+}	.9	1.0	1.6	2.2	1.5	1.2
Ni^{2+}	1.1	1.6	2.7	3.6	3.1	2.7
Zn^{2+}	1.4	1.3	2.0	3.1	2.6	2.3

[a] Metal ion sorption [CmgOH] = 1.0 g dm^{-3}, [PMS] = 10 × 10^{-3} mol dm^{-3}, [H$^+$] = 8 × 10^{-3} mol dm^{-3}, Time = 120 min, [GA] = 3.2 × 10^{-3} mol dm^{-3}, Temp. = 35 °C.
[b] A, B, C, D and E are graft copolymer samples prepared.

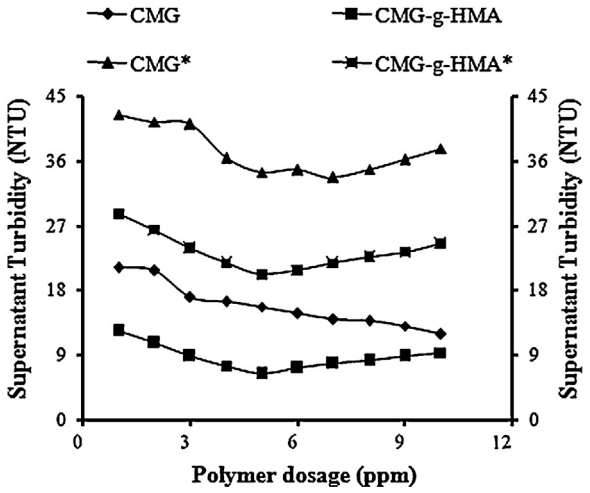


Fig. 5. Effect of polymer dosage on turbidity for coking coal and non coking coal*.

the dangling of poly [*N*-(hydroxymethyl) acrylamide] chains has better approachability (Deshmukh, Singh, & Chaturvedi, 1985) to the contaminant coal particles (Bratby, 1980). Hence increasing its flocculation capability. Here the bridging mechanism operates (Gregory, 1982), which involves binding or bridging individual particles to form flocs, hence increases its flocculation.

4. Conclusion

The thermal data show that the synthesized graft copolymer is thermally more stable than pure partially carboxymethylated guar gum. The synthesized graft copolymer i.e. partially carboxymethylated guar gum-g-*N*-(hydroxymethyl) acrylamide shows better results for swelling and flocculating properties in comparison to partially carboxymethylated guar gum, this could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of *N*-(hydroxymethyl) acrylamide might have taken place at hydroxyl group. The thermal analysis data shows that graft copolymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well for industrially.

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