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Studies on graft copolymerization of 2-acrylamidoglycolic acid on to partially carboxymethylated guar gum and physico-chemical properties

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ABSTRACT

An unreported graft copolymer of 2-acrylamidoglycolic acid with partially carboxymethylated guar gum has been synthesized under nitrogen atmosphere using peroxymonosulphate/thiourea redox pair at 40 °C. The effect of reaction conditions on grafting parameters i.e., grafting ratio, efficiency, conversion, add on, homopolymer and rate of grafting has been studied. Experimental results show that maximum grafting has been obtained at 0.1 g dm^{-3} concentration of partially carboxymethylated guar gum and 5.3×10^{-2} mol dm^{-3} concentration of 2-acrylamidoglycolic acid. It has been observed that grafting ratio, add on, conversion, efficiency and rate of grafting increase up to 5.0×10^{-3} mol dm^{-3} of hydrogen ion, 2.4×10^{-3} mol dm^{-3} of thiourea, 10×10^{-3} mol dm^{-3} of peroxymonosulphate and 40 °C of temperature. Grafted copolymer has been characterized by FTIR spectroscopy and thermogravimetric analysis. Physico-chemical properties of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid have been determined.

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1. Introduction

Modification of natural polymers by graft copolymerization is anticipated to be quite promising technique as it functionalises these biopolymer to their potential, imparting desirable properties onto them. Thus, in recent years, much attention has been paid on chemical modification of natural macromolecules through grafting (Kumar, Srivastava, & Behari, 2009; Mishra, Tripathy, Yadav, Sand, & Behari, 2010; Tripathy, Mishra, Yadav, Sand, & Behari, 2009). Partially carboxymethylated guar gum is a derivative of guar gum, which is a naturally occurring galactomannan polysaccharide isolated from the seed endosperm and having linear chain of β-D mannopyranose joined by (1–4) linking with a-D-galactopyranosyl units attached by 1,6 links in the ratio of 1:2 (Sinha & Kumria, 2001). Due to immense potential and low price, this versatile polymer is used as a vehicle for oral controlled release purpose (Skinner, Harcum, Barnum, & Guo, 1998). Guar gum and its derivatives find numerous other applications they act as major ingredients in drilling muds and fingering fluids in oil industry whereas in textile industry, help to improve printing quality (Turk and Schneider, 2000). Even though guar gum and its derivatives enjoy wide number of applications, however like other polysaccharides they are susceptible to biodegradation (Srivastava et al., 2007) which could be improved by grafting vinyl monomers onto them. Therefore partially carboxymethylated guar gum has been chosen a new type of polymeric backbone, which is water soluble. Various graft copolymers have been synthesized by graft copolymerization of vinyl monomers onto natural polymers in our laboratory (Mishra et al., 2009; Tripathy, Mishra, & Behari, 2009). Since 2-acrylamidoglycolic acid (AGA) is a cationic hydrophilic monomer with the availability of improved process for the synthesis and purification of 2-acrylamidoglycolic acid (poly 2-acrylamidoglycolic acid. 2-Acrylamidoglycolic acid (AGA) refers to a class of acrylamides containing –OH, –COOH and –CONH– functional groups (Rao et al., 2008).

2. Materials and methods

2.1. Materials

2-Acrylamidoglycolic acid (Aldrich), potassium peroxymonosulphate (Sigma), partially carboxymethylated guar gum (CMG) is gift sample from Hindustan Gums and Thiourea (E. Merck) were used as such. For maintaining the hydrogen ion concentration sulphuric acid (E. Merck) was used. The other chemical reagents were of analytical grade. All the solutions were prepared in triple distilled water. For flocculation studies, coking and non-coking coals were used received from Bokaro Steel Plant, India.

2.2. Procedure for copolymerization

For each experiment partially carboxymethylated guar gum solution are prepared by addition of weighed amount of partially carboxymethylated guar gum into reactor containing triple dis-

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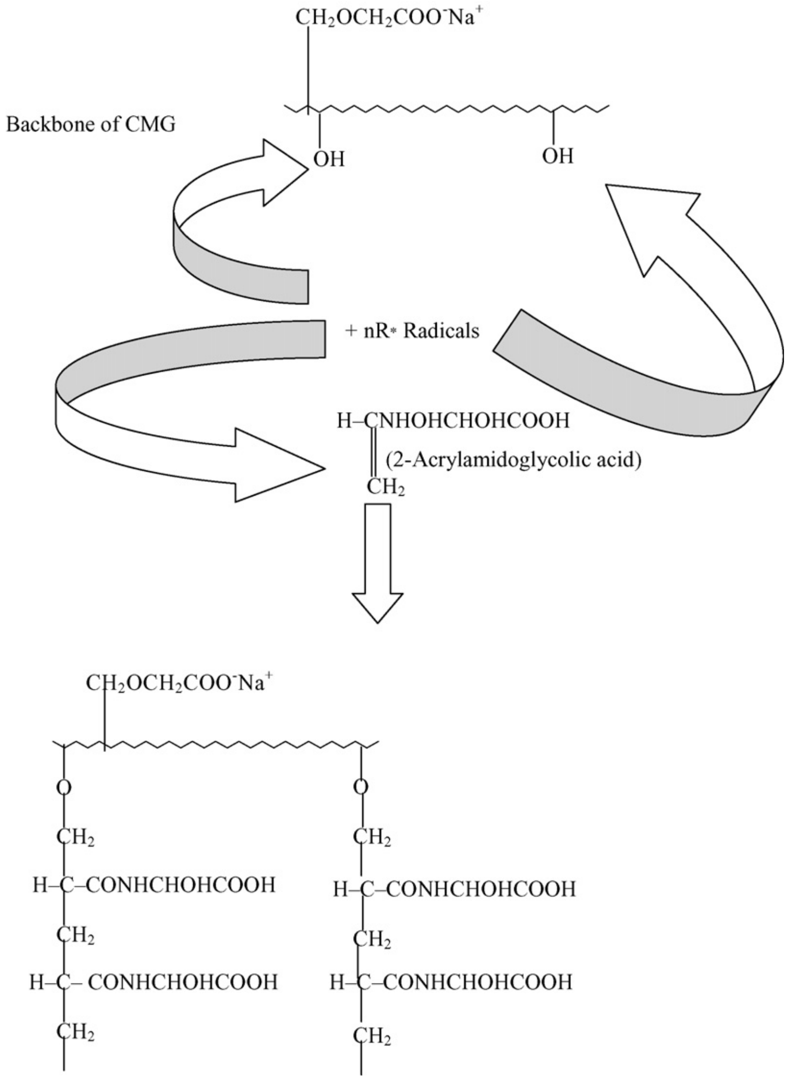


Scheme 1. Grafting of 2-acrylamidoglycolic acid on to partially carboxymethylated guar gum.

tilled water with rapid stirring in reactor (Scheme 1). The calculated amount of 2-acrylamidoglycolic acid, potassium peroxymonosulphate, thiourea, sulphuric acid and solutions has been added to the reactor at constant temperature and a slow stream of oxygen free nitrogen is passed. After 30 min, a known amount of deoxygenated potassium peroxymonosulphate solution is added to initiate the reaction and reaction is carried under oxygen free nitrogen atmosphere. After desired time period, the reaction is stopped by letting air into the reactor. The grafted sample is precipitated by pouring it in to water/methanol mixture (ratio 1:5). The grafted sample is separated by filtration and then dried and weighed.

3. Methods of characterization of partially carboxymethylated guar gum/partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid

3.1. FTIR analysis

The grafting reaction is confirmed by PERKIN ELMER FTIR model and infra red spectra of partially carboxymethylated guar gum and grafted samples have been recorded in the range from 500 to 4000 cm^{-1}.

3.2. TGA/DTA analysis

The thermograms have been recorded with NETZSCH-Geratebau GmbH thermal analyser in an inert atmosphere.

4. Study of physico-chemical properties

4.1. Swelling test

For the swelling studies, 0.02 g of each grafted sample synthesized by varying the concentration of 2-acrylamidoglycolic acid, has been taken and immersed in 20 ml of triple distilled water and kept undisturbed for 24 h. The surface water on the swollen graft copolymer has been removed by softly pressing it between the folds of filter paper. An increase in weight of graft copolymer has been recorded. Calculation of the percent swelling (P_S) and swelling ratio (S_R) has been made by the following expression (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000).

$$\text{Swelling ratio}\,(S_\mathrm{R}) = \frac{\text{weight of swollen sample} - \text{weight of dry sample}}{\text{weight of dry sample}}$$

$$\text{Percent swelling}\,(P_\mathrm{S}) = S_\mathrm{R} \times 100$$

4.2. *Metal ion sorption test*

The metal ion sorption study has been carried out by using samples of graft copolymers synthesized by varying the concentration of 2-acrylamidoglycolic acid from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. For this study, 0.02 g of graft copolymer has been taken in 10 ml of metal ion solution of known concentration, and kept for 24 h. The strength of sorbed metal ion has been determined by titrating the remaining metal ions. The results of sorption behavior of partially carboxymethylated guar gum and its grafted polymer with 2-acrylamidoglycolic acid have been determined in terms of different parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998) i.e., percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r).

$$\text{Percent uptake}\,(P_\mathrm{u}) = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion in feed}} \times 100$$

$$\text{Partition coefficient}\,(K_\mathrm{d}) = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion left in the solution}} \times \frac{\text{volume of solution (ml)}}{\text{weight of dry polymer}}$$

$$\text{Retention capacity}\,(Q_\mathrm{r}) = \frac{\text{amount of metal ion in the polymer (mEq.)}}{\text{weight of dry polymer (g)}}.$$

4.3. *Flocculation test*

In 1.0 l beaker, 200 ml of 1% (wt.) coal suspension was taken. The stirrer blade of the flocculator was dipped in the suspension. Under 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 withdrawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (supplied by ISO-TECH SYSTEM, Varanasi, India) to express the turbidity in nephelometric unit (N.T.U.).

4.4. *Resistance to biodegradability*

Resistance to biodegradability of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid has been measured in terms of viscosity and hence viscosity is calculated with the help of Ubbelohde capillary viscometer at constant temperature i.e., at 30 °C.

5. Results and discussion

5.1. *Estimation of grafting parameters*

Grafting parameters were calculated according to Fanta's (1973) definition.

$$\text{Grafting ratio}\,(\%G) = \frac{\text{grafted polymer}}{\text{weight of substrate}} \times 100$$

$$\text{Add on}\,(\%A) = \frac{\text{synthetic polymer}}{\text{graft copolymer}} \times 100$$

$$\text{Conversion}\,(\%C) = \frac{\text{polymer formed}}{\text{monomer charged}} \times 100$$

$$\text{Grafting efficiency}\,(\%E) = \frac{\text{grafted polymer}}{\text{polymer formed}} \times 100$$

$$\text{Homopolymer}\,(\%H) = 100 - \%E$$

Table 1
Effect of PMS concentration.

[PMS] × 10^{30} mol dm^{-3}	%*G*	%*E*	%*A*	%*C*	%*H*
6	189.1	63.6	62.5	30.4	36.3
8	219.3	66.8	69.9	39.6	34.1
10	292.8	70.6	74.7	48.1	29.3
12	190.1	64.5	66.1	35.1	35.6
14	140.3	53.9	58.6	30.4	35.9

[AGA] = 5.3×10^{-2} mol dm^{-3}, [TU] = 2.4×10^{-3} mol dm^{-3}, [CMG] = 1.0 g dm^{-3}, [H$^+$] = 5×10^{-3} mol dm^{-3}, Temp. = 40 °C, Time = 120 min.

5.2. *Determination of optimum reaction conditions*

The effect of variation of potassium peroxymonosulphate, thiourea, 2-acrylamidoglycolic acid, partially carboxymethylated guar gum (CMG), sulphuric acid, along with time and temperature on grafting parameters has been studied.

5.3. *Effect of concentration of peroxymonosulphate*

The effect of potassium peroxymonosulphate (PMS) concentration on graft copolymerization of 2-acrylamidoglycolic acid onto partially carboxymethylated guar gum has been studied by varying the concentration of peroxymonosulphate from 6×10^{-3} to 14×10^{-3} mol dm^{-3}. The results are presented in Table 1. The grafting ratio, add on, efficiency and conversion have been found to increase continuously on increasing the concentration of PMS from 6×10^{-3} to 14×10^{-3} mol dm^{-3} and homopolymer formation decreases. The increment in grafting parameters may be due to the progressive reduction of peroxymonosulphate by thiourea, which produces primary free radicals i.e., $\mathrm{R_1S^\bullet}$ and $\mathrm{SO_4^{\bullet -}}$ (Kumar et al., 2009) and these primary free radicals generate more number of active sites on polymeric backbone, to which monomer addition takes place.

5.4. *Effect of thiourea concentration*

The variation of concentration of thiourea (TU) from 0.8×10^{-3} to 4.0×10^{-3} mol dm^{-3} reveals that of grafting ratio, add on, conversion and efficiency increase on increasing the thiourea concentration up to 2.4×10^{-3} mol dm^{-3} due to availability of more primary free radicals ($\mathrm{R_1S^\bullet}$ and $\mathrm{SO_4^{\bullet -}}$), which might be formed due to progressive reduction of PMS 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 the premature termination of 2-acrylamidoglycolic acid radicals which will cause to give more homopolymer.

5.5. *Effect of hydrogen ion concentration*

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 3.0×10^{-3} to 7.0×10^{-3} mol dm^{-3} results are given in Table 2. It has been observed from Table 2 and found that grafting ratio, add on, conversion and efficiency increase due to protonation of thiourea which takes place on increasing the hydrogen ion concentration up to

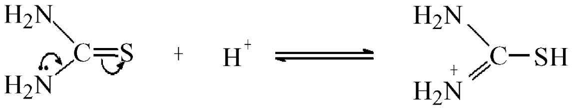
Table 2
Effect of $[H]^+$ concentration.

$[H^+] \times 10^3$ mol dm^{-3}	%*G*	%*E*	%*A*	%*C*	%*H*
3	180.1	64.2	62.8	30.4	35.7
4	230.3	66.3	66.3	40.1	33.6
5	292.8	70.6	74.7	48.1	29.3
6	261.1	64.9	72.3	46.5	35.6
7	140.5	57.3	58.6	28.5	42.6

[AGA] = 5.3×10^{-2} mol dm^{-3}, [PMS] = 10×10^{-3}, Time = 120 min, [CMG] = 1.0 g dm^{-3}, [TU] = 2.4×10^{-3} mol dm^{-3}, Temp. = 40 °C.

5.0×10^{-3} mol dm^{-3} which in turn protonated species reacts with PMS to give more primary free radicals.

The active species (R_1SH) reacts with PMS to give more primary free radicals.



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

But on further increasing the concentration of H^+ ions beyond 5.0×10^{-3} mol dm^{-3}, the grafting parameters decrease while homopolymer increases. This effect could be explained as

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

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

5.6. *Effect of 2-acrylamidoglycolic acid*

The effect of concentration of 2-acrylamidoglycolic acid on grafting parameters has been investigated by varying the concentration of 2-acrylamidoglycolic acid (AGA) from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. It has been observed that grafting ratio and add on (5.3×10^{-2} mol dm^{-3}) and efficiency increase on increasing the concentration up to 6.6×10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease. 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 neighboring molecules leading lower of termination. But on further increasing the concentration of 2-acrylamidoglycolic acid, the grafting parameters decrease due to formation of more homopolymer.

5.7. *Effect of partially carboxymethylated guar gum concentration*

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 1.6 g dm^{-3}) on grafting parameters like grafting ratio and add on. The results are presented in Fig. 1. It has been observed that the grafting parameters decrease continuously on increasing the concentration of partially carboxymethylated guar gum. This is due to the fact that as the concentration of partially carboxymethylated guar gum increases, the viscosity of reaction medium increases, which hinders the movement of free radicals.

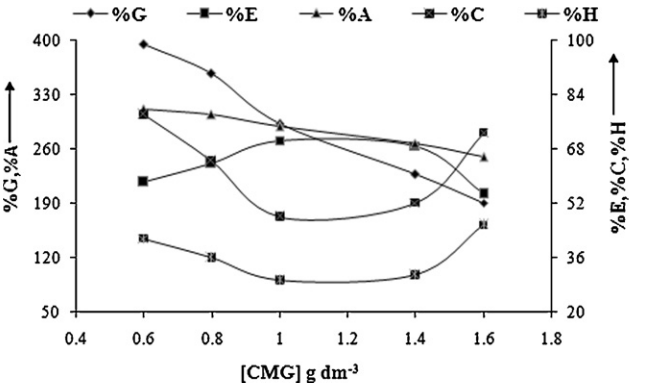


Fig. 1. Effect of concentration of partially carboxymethylated guar gum. [AGA] = 5.3×10^{-2} mol dm^{-3}, [PMS] = 10×10^{-3} mol dm^{-3}, Time = 120 min, $[H^+]$ = 5×10^{-3} mol dm^{-3}, [TU] = 2.4×10^{-3} mol dm^{-3}, Temp. = 40 °C.

5.8. *Effect of time period*

The effect of time duration on grafting reaction has been studied by varying the time period from 60 to 180 min. On increasing the time period from 60 to 120 min the availability of more active species results into the increase in grafting ratio (%*G* = increases from 199.8 to 292.8), efficiency and add on. But further increase in time period, the decrement in these parameters (up to %*G* = 100) is observed which might be due to termination of growing grafted chains.

5.9. *Effect of temperature*

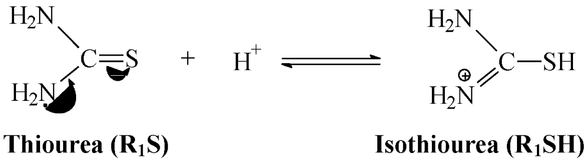
For all grafting parameters at different temperatures. It has been observed on changing the temperature from 30 to 50 °C, the grafting parameters increase up to 40 °C and there after decrease. The increment in grafting parameters up to 40 °C is attributed due to the increase in the formation of active sites on account of enhanced production of primary free radicals.

The decrement in grafting parameters 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) The increase in temperature may lead to the decomposition of PMS 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.

5.10. *Mechanism*

A tentative mechanism has been proposed on the basis of results obtained. Initially thiourea reacts with hydrogen ion to give protonated species (R_1SH), which reacts with peroxymonosulphate to form a complex. The complex dissociates to give primary free radicals $R_1S^\bullet$ and $SO_4^{\bullet -}$. These radicals abstract hydrogen atom from the partially carboxymethylated guar gum (CMGOH) molecules, producing macro radicals of partially carboxymethylated guar gum. The monomer molecules, which are in close vicinity of the reaction sites, become acceptors of partially carboxymethylated guar gum radicals resulting in chain initiation and thereafter themselves become free radical donor to neighboring molecules. In this way grafted chains grow and terminate by coupling to give graft copolymer. The probable reaction mechanism can be represented as.



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

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

Initiation:

$\text{CMGOH} + R^{\bullet} \rightarrow \text{CMGO}^{\bullet} + \text{RH}$

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

[where $R^{\bullet} = R_1S^{\bullet}$ or $SO_4^{\bullet -}$, CMGOH = partially carboxymethylated guar gum and M = 2-acrylamidoglycolic acid]

Propagation:

$\text{CMGO}^{\bullet} + M \rightarrow \text{CMGOM}_1^{\bullet}$

$\text{CMGOM}_1^{\bullet} + M \rightarrow \text{CMGOM}_2^{\bullet}$

$\text{CMGOM}_2^{\bullet} + M \rightarrow \text{CMGOM}_3^{\bullet}$

$\text{CMGOM}_{n-1}^{\bullet} + M \rightarrow \text{CMGOM}_n^{\bullet}$

$RM_1^{\bullet} + M \rightarrow RM_2^{\bullet}$

$RM_2^{\bullet} + M \rightarrow RM_3^{\bullet}$

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

Termination:

$\text{CMGOM}_n^{\bullet} + \text{CMGOM}_m^{\bullet} \rightarrow \text{Graftcopolymer}$

$\text{CMGOM}_n^{\bullet} + RM_n^{\bullet} \rightarrow \text{Graftcopolymer}$

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

5.10.1. Evidence of grafting

5.10.1.1. IR spectroscopy of partially carboxymethylated guar gum partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid. The IR spectra of ungrafted and grafted samples have been recorded with JASCO FTIR-5300 model in the range from 500 to 4000 cm^{-1} to provide the proof of the grafting. The infra red spectra analyses has been utilized to prove grafting, for this IR of partially carboxymethylated guar gum (Tripathy et al., 2008) and partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid (Fig. 2) have been recorded in the range from 500 to 4000 cm^{-1}. On comparing the IR spectra of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid, a band at 3450.0 cm^{-1} is due to OH stretching vibration in the spectrum of partially carboxymethylated guar gum. It is observed that there is variation in intensity of OH stretching vibration and shifting of this peak from 3450.0 to 3452.0 cm^{-1} appeared in partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band of amide I at 1649.0 cm^{-1} due to $>$C=O stretching vibration, and at 1424.0 cm^{-1} due to –CN stretching vibration of monomer molecule 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 from the spectrum of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid showed that grafting might have taken place on OH sites of partially carboxymethylated guar gum.

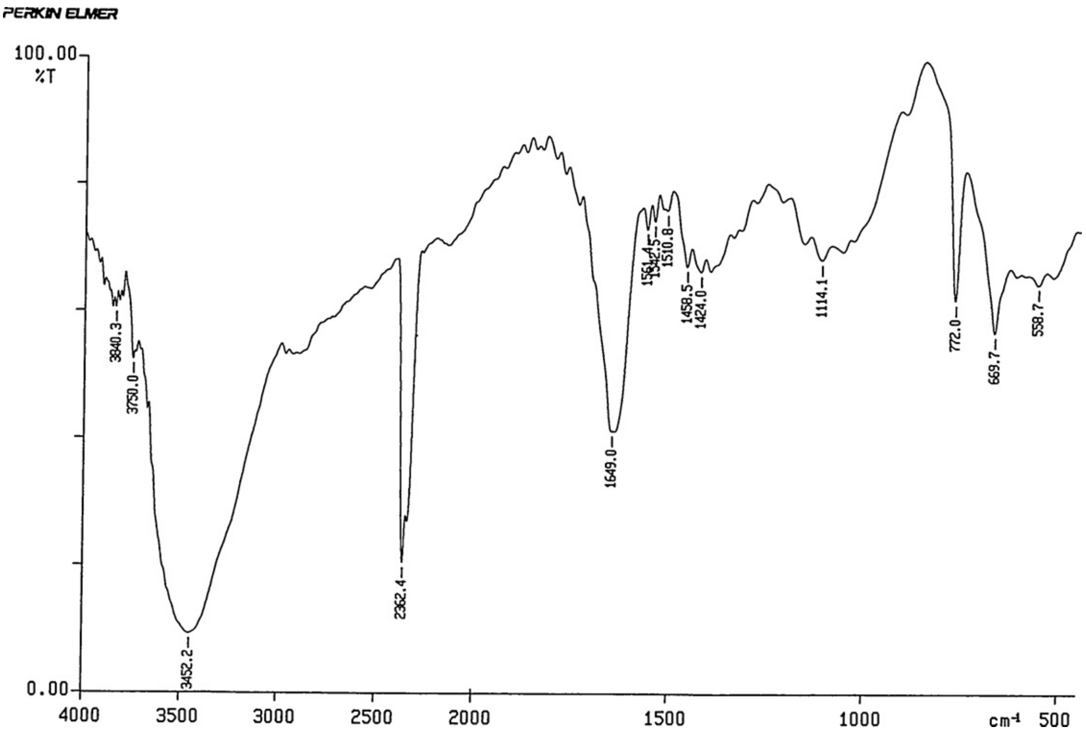


Fig. 2. IR spectrum of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid.

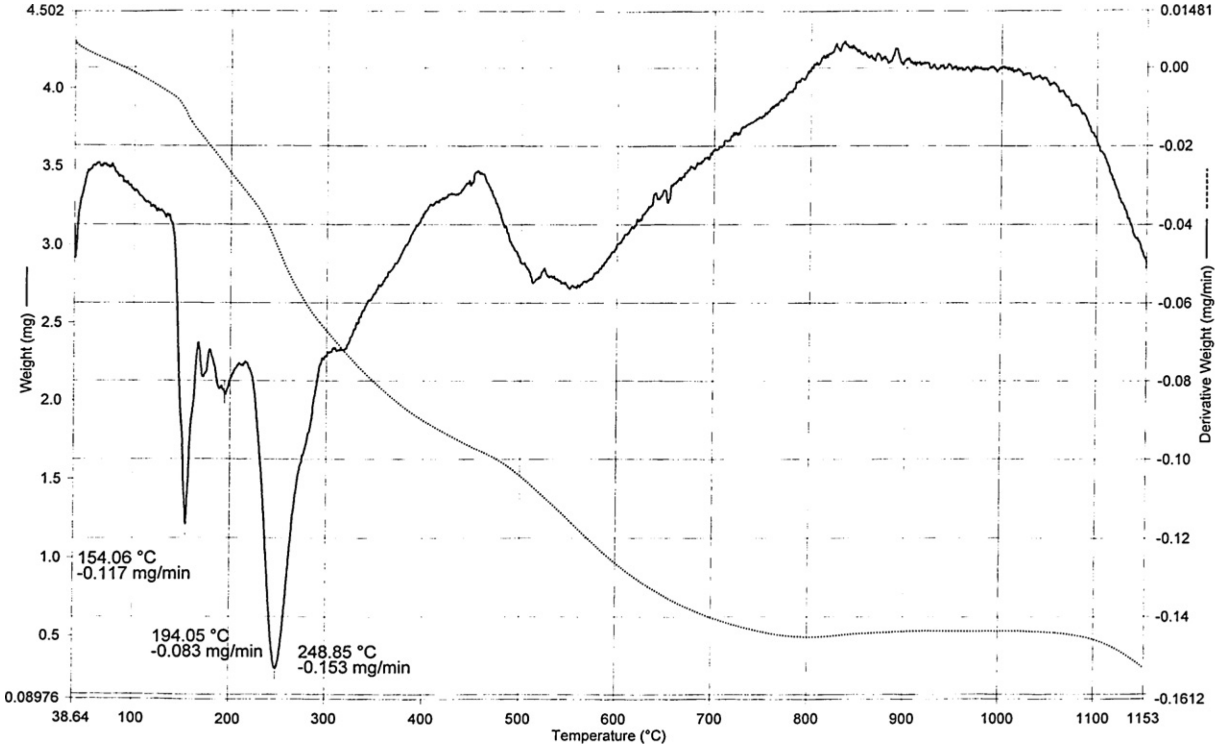


Fig. 3. Thermogravimetric trace of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid.

5.10.2. *Thermal analysis of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid*

Thermogravimetric curve of partially carboxymethylated guar gum (Tripathy et al., 2008) shows single step degradation. The weight loss 1.5% is due to loss absorbed water at 54.9 °C. The polymer decomposition temperature has been found at 75.9 °C. The weight loss increases with increase in temperature from 75.9 to 184.2 °C and attains maximum at 284.2 °C. The integral procedural decomposition temperature (IPDT) is 189.5 °C. $T_{\max}$, the temperature at which maximum degradation occurred is 268 °C and final decomposition temperature has been observed at about 900 °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 pure partially carboxymethylated guar gum and its graft copolymers has also been determined by calculating IPDT values using following equation (Doyle, 1961). The area under the curve divided by the total area is the total curve area, A^*, is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, T_{A^*}, by following equation:

$$T_{A*} = (T_{\text{end}} - T_{\text{initial}})A * + T_{\text{initial}} \qquad (1)$$

T_{A^*} represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing X-axis up to T_{A^*} and the Y-axis mass fraction remaining at T_{end}. K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in Eq. (1). Partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid (Fig. 3) starts to degrade at about 110.5 °C. The rate of weight loss increases with increase in temperature from 110.5 to 157.9 °C and attains maximum at 283.3 °C. Thermogravimetric curve of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid shows three step degradations. First $T_{\max}$, 154.1 °C is due to elimination of CO_2 molecule which also confirmed by a peak appeared in DTA curve of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid at near 165 °C. The second $T_{\max}$, is 194.1 °C is due to elimination of –NHCHOHCOOH group, confirmed by a peak appeared at about 210 °C in DTA curve and the third $T_{\max}$ at 248.9 °C is due to elimination of CO molecule from pendent chains attached to the partially carboxymethylated guar gum. The integral procedural decomposition temperature and final decomposition temperature have been found at about 271.97 and 1120 °C respectively. On comparing the thermograms of parent backbone of partial carboxymethylated guar gum and graft copolymer (partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid), it has been observed that final and integral procedural decomposition have been found to be higher. The higher values of final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) indicate that is more stable.

6. The physico-chemical properties

6.1. *Swelling studies*

The percent swelling and swelling ratio increase with increase in grafting, which is dependent upon monomer concentration. It has been observed that a maximum percent swelling of 450% occurs when grafting ratio is 292%. Since 2-acrylamidoglycolic acid is a hydrophilic monomer, it increases the water absorbing capacity and water retention character of graft copolymer. The long pendant chains of 2-acrylamidoglycolic acid are responsible for maximum hydrophilic character (Nasef, Saidi, Nor, & Foo, 2000) in graft copolymer thereby increasing the value of swelling ratio.

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

Hydrophilic–hydrophobic balance and nature of monomer are major factors those effect the metal ion uptake (Lehto, Vaaramaa,

Table 3
Metal ion sorption.

Sample	$[AGA] \times 10^2$ mol dm^{-3}	%G	Percent uptake (P_u)			Partition coefficient (K_d)			Retention capacity (Q_r)		
			Pb^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Pb^2	Ni^{2+}	Zn^{2+}
CMG	–	–	2.4	1.4	0.8	5.1	2.0	2.1	0.5	0.3	0.3
A	2.6	189.1	4.5	3.7	2.5	11.5	9.7	8.4	1.6	1.3	1.2
B	4.0	211.3	7.8	6.2	3.8	17.5	15.8	11.1	2.0	1.8	1.3
C	5.3	292.8	13.5	9.8	7.2	36.8	28.2	22.3	3.6	2.9	2.4
D	6.6	250.1	9.9	8.2	6.5	23.8	21.3	19.5	2.9	2.2	1.9
E	8.0	201.3	8.3	6.9	5.0	20.5	20.0	14.1	1.9	2.0	1.7

where CMG = partially carboxymethylated guar gum, A, B, C, D and E = Graftcopolymers. $[AGA] = 5.3 \times 10^{-2}$ mol dm^{-3}, $[PMS] = 10 \times 10^{-2}$ mol dm^{-3}, $[CMG] = 1.0$ g dm^{-3}, $[MEA] = 2.4 \times 10^{-3}$ mol dm^{-3} $[H^+] = 5 \times 10^{-3}$ mol dm^{-3}, Temp. = 40 °C, Time = 120 min.

Vesterinen, & Tenhu, 1998). These functionalities can be tailored and incorporated by grafting to retain ion by polymer analogous reaction or by simple chelation absorption due to opening of polymer matrix or pores created. Out of these possibilities, all may contribute in the metal ion sorption, though extent of contribution of any factor may be different (Inou, Baba, & Yoshizuka, 1993). However functional group incorporated with the help of grafting by its ability to interact with metal ions may play more important role in determination of selectivity and quantum of metal ion uptake (Sheng, Ting, Chen, & Hong, 2004). Three metal ions have been chosen (Zn^{2+}, $Ni^{2+}$and Pb^{2+}) for the study of metal ions sorption and the amount of metal uptake was calculated by titrating the unabsorbed metal ions (all the solutions were made in triple distilled water). The increment in all these parameters might be due to grafting of 2-acrylamidoglycolic acid which accounts for the higher sorption of these divalent cations through a chelating reaction (Onsoyen & Skaugrud, 1990) as shown and the results are given in Table 3.

6.3. Flocculation performance

At the time of mixing, concentration of flocculants was very low so that to make a uniformly dispersed polymer solution and coal powder was uniformly suspended in the water by stirring. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone xanthan gum and graft copolymer of partially carboxymethylated guar gum with 2-acrylamidoglycolic acid. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in (Fig. 4). It has been found that grafted copolymer (partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid) shows better performance than partially carboxymethylated guar gum itself which could be explained due to the fact that in grafted copolymer, the dangling of poly (2-acrylamidoglycolic acid) chains have better approachability (Deshmukh et al., 1985) to the contaminant coal particles. Here the bridging mechanism operates (Gregory, 1982), which involves binding or bridging individual particles to form flocs, hence increases its flocculation capability. By grafting of poly 2-acrylamidoglycolic acid onto partially carboxymethylated guar gum, efficient flocculant has been obtained.

6.4. Resistance to biodegradability

From efflux time of polymer solution (t) and that of solvent 1.0 M $NaNO_3$ (t_o), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of partially carboxymethylated guar gum-g-2-acrylamidoglycolic acid is lower than partially carboxymethylated guar gum (Fig. 5). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Singh et al., 1989). Partially carboxymethylated guar gum, like other polysaccharide solutions, is highly prone to biodegradation, and it was found that its solution after 72 h of its preparation starts degrading and during 10 days the solution showed considerable loss of viscosity (Fig. 5, Line A). The graft copolymer solution was subjected for same type of study for biodegradation, and it has been observed that graft copolymer solution showed no loss of viscosity up to 10 days (Fig. 5, Line B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others (Ungeheur, Bewersdorff, & Singh, 1989). This is in an agreement with the fact that by incorporating relatively poly (2-acrylamidoglycolic acid) chains in graft copolymer it can be made less susceptible to bacterial attack (Seaman, 1980).

Thus, it can be concluded that, by incorporation of poly(2-acrylamidoglycolic acid) graft onto partially carboxymethylated

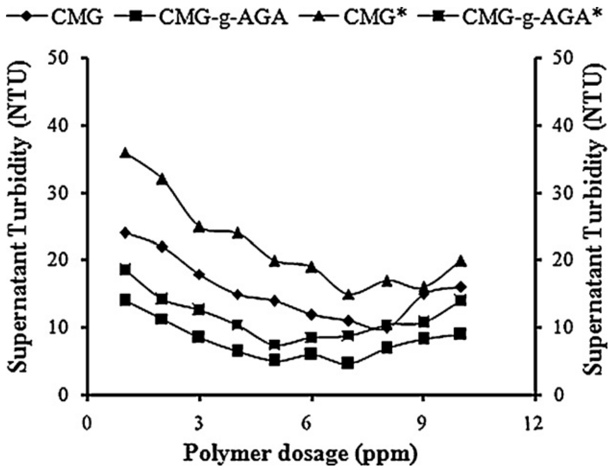


Fig. 4. Effect of polymer dosage on turbidity for coking coal and non coking coal*.

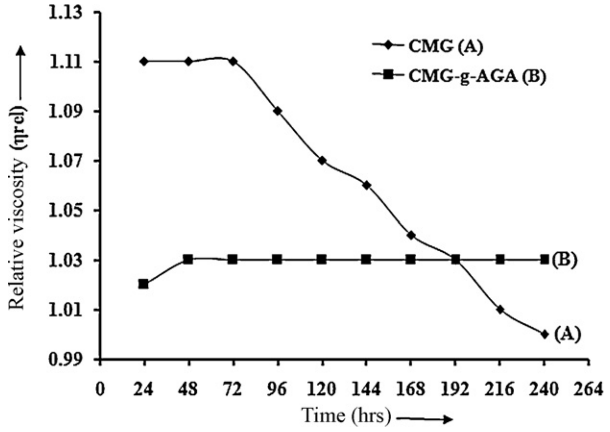


Fig. 5. Relative viscosity vs. time period to study biodegradation of partially carboxymethylated guar gum and graft copolymer.

guar gum through graft copolymerization biodegradation can be minimized.

7. 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-2-acrylamidoglycolic acid shows better results for swelling, metal ion sorption and flocculating properties in comparison to partially carboxymethylated guar gum, thus could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of 2-acrylamidoglycolic acid might have taken place at hydroxyl group, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft copolymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well industrially.

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References

Abd EL-Rehim, H. A., Hegazy EL-Sayed, A., & Ali, A. M. (2000). Selective separation of some heavy metals by poly (vinyl alcohol)-grafted membranes. *Journal of Applied Polymer Science*, *76*, 125–132.

Deshmukh, S. R., Singh, R. P., & Chaturvedi, P. N. (1985). The turbulent drag reduction by graft copolymer of guar gum and polyacrylamide. *Journal of Applied Polymer Science*, *30*, 4013.

Doyle, C. D. (1961). Estimating thermal stability of experimental polymers by empirical thermogravimetric analysis. *Analytical Chemistry*, *33*, 77.

Fanta, G. F. (1973). Block and graft copolymerization. In R. J. Ceresa (Ed.), *Synthesis of graft and block copolymers of starch* (pp. 1–27). New York: Wiley-Interscience.

Gregory, J. (1982). Polymer flocculation in flowing dispersions. In T. F. Tadros (Ed.), *The effect of polymers on dispersion properties* (pp. 301–321). London: Academic Press.

Inou, K., Baba, Y., & Yoshizuka, K. (1993). Adsorption of metal ions on chitosan and crosslinked copper (II)-complex chitosan. *Bulletin of the Chemical Society of Japan*, *66*, 2915–2921.

Kumar, R., Srivastava, A., & Behari, K. (2009). Synthesis and characterization of polysaccharide based graft copolymer by using potassium peroxymonosulphate/ascorbic acid as an efficient redox initiator in inert atmosphere. *Journal of Applied Polymer Science*, *112*(3), 1407–1415.

Lehto, J., Vaaramaa, K., Vesterinen, E., & Tenhu, H. (1998). Uptake of zinc, nickel, and chromium by N-isopropyl acrylamide polymer jells. *Journal of Applied Polymer Science*, *68*, 355–362.

Mishra, M. M., Tripathy, J., Yadav, M., Sand, A., & Behari, K. (2010). Water Soluble Graft copolymer (K-carrageenan-g-N-vinyl formamide): Preparation. *Characterization and Application Carbohydrate Polymers*, *71*, 524–534, 80, 235–241.

Nasef, M. M., Saidi, H., Nor, H. M., & Foo, O. M. (2000). Swelling behaviour cation exchange membranes by radiation-induced graft copolymerization of styrene onto PFA copolymer films. II. Charactarization of sulfonated graft copolymer membranes. *Journal Applied Polymer Science*, *76*, 1–11.

Onsoyen, E., & Skaugrud, Q. (1990). Metal recovery using chitosan. *Journal of Chemical Technology & Biotechnology*, *49*, 395–404.

Rao, K. S. V., Chung, I., & Ha, C. S. (2008). Synthesis and characterization of poly (acrylamidoglycolic acid) grafted onto chitosan and its polyelectrolyte complexes with hydroxyapatite. *Reactive and Functional Polymer*, *68*, 943–953.

Rivas, B. L., Maturana, H. A., Molina, M. J., Gomez-Anton, M. R., & Pierola, I. F. (1998). Metal ion binding properties of poly (N-vinylimidazole) hydrogels. *Journal of Applied Polymer Science*, *67*, 1109–1118.

Seaman, J. K. (1980). In R. L. Davidson (Ed.), *Handbook of water soluble gums and resins* (pp. 6–9). New York: McGraw-Hill.

Sheng, P. X., Ting, Y. P., Chen, J. P., & Hong, L. (2004). Sorption of lead, copper, cadmium, zinc, and nickel by marine algal biomass: Characterization of biosorptive capacity and investigation of mechanisms. *Journal of Colloid and Interface Science*, *275*, 131–141.

Sinha, V. R., & Kumria, R. (2001). Polysaccharides in colon-specific drug delivery. *International Journal of Pharmaceutics*, *Vol. 224*, 19–38.

Skinner, G. W., Harcum, W. W., Barnum, P. E., & Guo, J. H. (1998). *Proceedings of annual meeting of the American* Association of Pharmaceutical Scientists, (p. 514).

Srivastava, A., Tripathy, J., Mishra, M. M., & Behari, K. (2007). Modification of guar gum through graft copolymerization of 4-vinyl pyridine using potassium peroxymonosulphate/ascorbic acid redox pair. *Journal of Applied Polymer Science*, *106*, 1353.

Tripathy, J., Mishra, D. K., Mishra, M. M., Srivastava, A., & Behari, K. (2008). Synthesis of partially carboxymethylated guar gum-g-4-vinyl pyridine and study of its water swelling, metal ion sorption and flocculation behaviour. *Carbohydrate Polymers*, *78*, 462–472.

Tripathy, J., Mishra, D. K., Yadav, M., Sand, A., & Behari, K. (2009). Modification of κ-carrageenan by graft copolymerization of methacrylic acid: Synthesis and applications. *Journal of Applied Polymer Science*, *114*(3), 3896–3905.

Tripathy, J., Mishra, D. K., & Behari, K. (2009). Graft copolymerization of N-vinylformamide onto sodium carboxymethylcellulose and study of its swelling, metal ion sorption and flocculation behaviour. *Carbohydrate Polymers*, *75*, 604–639.

Turk, S. S., & Schneider, R. (2000). Printing properties of a high substituted guar gum and its mixture with alginate. *Dyes and Pigments*, *47*, 269–275.

Ungeheur, S., Bewersdorff, H. W., & Singh, R. P. (1989). Turbulent drag effectiveness and shear stability of xanthan-gum-based graft copolymers. *Journal of Applied Polymer Science*, *37*, 2933–2948.