A Study Toward the Physicochemical Properties of Graft Copolymer (Partially Carboxymethylated Guar Gum-*g*-N,N′-dimethylacrylamide): Synthesis and Characterization

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ABSTRACT: Unreported graft copolymer of N,N′-dimethylacrylamide (DMA) with partially carboxymethylated guar gum (CmgOH) has been synthesized and the reaction conditions have been optimized for affording maximum grafting using a potassium peroxymonosulphate (PMS)/thiourea (TU) redox initiators under nitrogen atmosphere. The study of graft copolymerization has been performed to observe maximum value of grafting parameters except percentage of homopolymer by varying the concentrations of DMA, PMS, and TU. The grafting parameters increase continuously on increasing the concentration of DMA from 8×10^{-2} to 24×10^{-2} mol dm^{-3}, PMS from 5×10^{-3} to 21×10^{-3} mol dm^{-3}, and TU from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3}. The optimum temperature and time for grafting of DMA onto CmgOH were found to be 35°C and 120 min, respectively. The water-swelling capacity of graft copolymer is investigated. Flocculation property for both coking and noncoking coals is studied for the treatment of coal mine waste water. The graft copolymer is characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 974–981, 2010

Key words: graft copolymer; partially carboxymethylated guar gum; N,N′-dimethylacrylamide; swelling; flocculation

INTRODUCTION

Modification of natural polymers by graft copolymerization of vinyl monomers is anticipated to be quite promising technique, as it functionalizes biopolymers to impart desirable properties onto them. Thus, in recent years, much attention has been paid on chemical modification of natural macromolecules.[1–5] 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,N′-dimethylacrylamide). Partially carboxymethylated guar gum (CmgOH) has been chosen as backbone, which is derivative of naturally occurring guar gum and constituted of galactomannan polysaccharide isolated from the seed endosperm and having linear chain of β-D-mannopyranose joined by (1-4) linking with α-D-galactopyranosyl units[6] attached by 1,6 links in ratio of 1 : 2.

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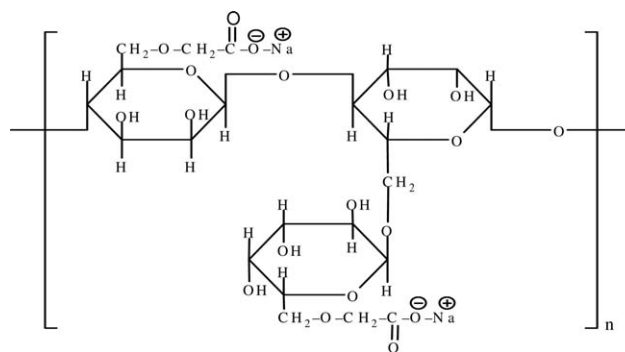
Because of the immense potential and low price, this versatile polymer is used as a vehicle for oral-controlled release purpose.[7] Guar gum and its derivatives find numerous other applications, such as in oil industry they also act as major ingredients in drilling muds and fingering fluids whereas in textile industry help to improve printing quality.[8] Even though guar gum and its derivatives enjoy wide range of applications, however, like other polysaccharides they suffer from their drawback like easier susceptibility of microbial attack[9]; 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-base advanced materials, but reports on grafting

onto the CmgOH are scantily available in the light of its versatile applications. This work is carried out with an aim to tailor CmgOH-based hybrid material by grafting of N,N′-dimethylacrylamide (DMA), which is hydrophilic[10] and biocompatible[11] in nature. DMA is one of the smart materials that has received considerable attention due to its hydrogel-forming property.[12] Because of its hydrophilic and biocompatible nature, it finds numerous applications in the medical and pharmaceutical fields,[13,14] including contact lenses[15] and in drug delivery.[16] Taking in mind all of these fascinating applications of DMA and CmgOH, an attempt has been made to graft hitherto unreported DMA onto CmgOH. The resulting graft copolymer shows better enhancement in the properties toward flocculation and water-swelling capacity than initial polymer.

EXPERIMENTAL

Materials

N,N′-dimethylacrylamide (DMA, Sigma-Aldrich, Gillingham, Dorset, U.K.) was distilled under reduced pressure at 14 mmHg and 50°C and only middle fraction was used. Partially carboxymethylated guar gum (CmgOH) was received as a gift sample from Hindustan Gums and Chemicals (India). Potassium peroxymonosulphate (PMS) was received from Du Pont (USA). Thiourea (TU, E. Merck, India) was used as such. For maintaining hydrogen ion concentration, sulfuric acid (E. Merck, India) is used. All the solutions were prepared in triple distilled water. The other chemicals used are of analytical grade and used as such without further purification. For the flocculation, coking and noncoking coals used were received from Steel Plant Bokaro (India).

Procedure for graft copolymerization

All the reactions were carried out in three-necked flask under oxygen-free nitrogen atmosphere. For each experiment, CmgOH solution has been prepared by adding weighed amount of CmgOH into the reactor containing triple distilled water with rapid stirring. The calculated amount of DMA, PMS, thiourea (TU), and sulphuric acid solutions has been added to the reactor at constant temperature and a slow stream of nitrogen is passed continuously for half-an-hour; a known amount of deoxygenated-PMS solution is added to initiate the reaction. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated out by pouring it into water/methanol mixture ratio (1 : 5). The grafted sample has been separated by filtration and then dried and weighed.

Separation of homopolymer

Poly(DMA) remained in the filtrate. To the filtrate, a pinch of hydroquinone has been added, and then, it is concentrated by distillation under reduced pressure. The concentrated solution is poured into the pure methanol to precipitate out homopolymer of DMA. The poly(DMA) is separated, dried, and weighed.

Estimation of grafting parameters

The grafting parameters have been calculated by using Fanta's expressions[17,18]:

$$\text{Grafting ratio } (\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Add on } (\%A) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion } (\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Grafting efficiency } (\%E) = \frac{\text{Polymer in graft}}{\text{Polymer formed}} \times 100$$

$$\text{Homopolymer } (\%H) = 100 - \%\text{Grafting efficiency.}$$

Study of properties

Swelling

For swelling study, different samples of graft copolymer have been synthesized at different concentrations of DMA from 8×10^{-2} to 24×10^{-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[19]:

$$P_S = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}} \times 100$$

$$S_T = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}}.$$

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 the 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-anhour. 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, Varanasi, India] to express the turbidity in nephelometric unit (N.T.U.).

Method of characterization of partially carboxymethylated guar gum-g-N,N′-dimethylacrylamide

IR spectroscopy

The IR spectra of CmgOH and grafted samples have been recorded with JASCO FT/IR-5300 model in the range 500 to 4000 cm^{-1} to provide the proof of the grafting.
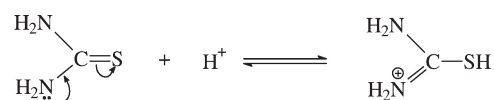
Thermogravimetric analysis

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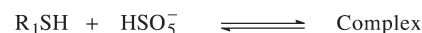
RESULTS AND DISCUSSIONS

Mechanism

A mechanism has been proposed on the basis of results obtained. Initially TU reacts with hydrogen ion to give protonated species, which react with PMS to form a complex.[20] The complex dissociates to give primary free radicals $R_1S^{\bullet}$ and $SO_4^{-\bullet}$ represented by $R^{\bullet}$. These radicals abstract hydrogen atoms from the CmgOH molecules, producing macroradicals of CmgOH. The monomer molecules, which are at close vicinity of the reaction sites, become acceptors of CmgOH radicals, resulting in chain initiation and thereafter themselves become free radical donors to neighboring molecules.[21] In this way, grafted chains grow and terminate by coupling to give graft copolymer. The reaction mechanism can be represented as follows:
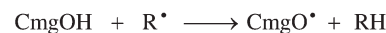
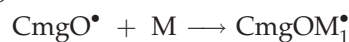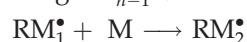**Thiourea (R_1S)**   **Isothiourea (R_1SH)**

$$R_1SH + HSO_5^- \rightleftharpoons Complex$$

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

Initiation

$$CmgOH + R^{\bullet} \longrightarrow CmgO^{\bullet} + RH$$

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

where $R^{\bullet}$ is the $R_1S^{\bullet}$ or $SO_4^{-\bullet}$, CmgOH is the partially carboxymethylated guar gum, and M is the monomer.
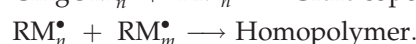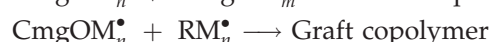
Propagation

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

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

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

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

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

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

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

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

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

Termination

$$CmgOM_n^{\bullet} + CmgOM_m^{\bullet} \longrightarrow Graft\ copolymer$$

$$CmgOM_n^{\bullet} + RM_n^{\bullet} \longrightarrow Graft\ copolymer$$

$$RM_n^{\bullet} + RM_m^{\bullet} \longrightarrow Homopolymer.$$

Determination of optimum grafting conditions

The optimum reaction conditions for affording maximum percentage of grafting have been established in the case of grafting of DMA onto CmgOH by using PMS and TU redox initiators in the presence of hydrogen ion (H^+) with the effect of time and temperature.

Effect of N,N′-dimethylacrylamide

The effect of concentration of DMA on grafting parameters has been investigated by varying the concentration of DMA from 8.0×10^{-2} to 24.0×10^{-2} mol dm^{-3}, and the results are summarized in Table I. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration up to 16×10^{-2} mol dm^{-3} and thereafter grafting parameters decrease. However, the formation of homopolymer

TABLE I
Effect of N,N′-Dimethylacrylamide

DMA × 10^{-2} (mol dm^{-3})	%G	%E	%A	%C	%H
8	144.7	54.5	59.1	20.8	45.5
12	157.6	55.7	64.2	15.4	44.3
16	190.3	60.2	65.6	13.7	39.9
20	164.5	56.9	62.2	9.5	43.1
24	137.1	52.9	57.8	6.7	47.0

[CmgOH] = 1.0 g dm^{-3}; [PMS] = 13 × 10^{-3} mol dm^{-3}; Time = 120 mins; [TU] = 3.2 × 10^{-3} mol dm^{-3}; [H$^+$] = 5.5 × 10^{-3} mol dm^{-3}; Temperature = 35°C.

TABLE II
Effect of Thiourea

Thiourea × 10^{3} (mol dm^{-3})	%G	%E	%A	%C	%H
1.6	152.0	57.5	60.3	10.4	42.6
2.4	165.1	58.2	62.3	11.6	41.8
3.2	190.3	60.2	65.6	13.7	39.9
4.0	168.7	55.2	62.8	12.9	44.8
4.8	141.0	51.0	58.5	11.1	48.9

[CmgOH] = 1.0 g dm^{-3}; [DMA] = 16 × 10^{-2} mol dm^{-3}; Time = 120 mins; [PMS] = 13 × 10^{-3} mol dm^{-3}; [H$^+$] = 5.5 × 10^{-3} mol dm^{-3}; Temperature = 35°C.

shows a reverse trend with respect to grafting efficiency. This behavior is attributed due to the accumulation of monomer molecules, which are at close proximity of polymeric backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of CmgOH macroradicals, resulting in chain initiation and thereafter themselves become free radical donors to the neighboring molecules leading to lower of termination. However, on further increasing the concentration of DMA beyond 16 × 10^{-2} mol dm^{-3}, the results are found to decrease due to increment in the viscosity of reaction mixture, which facilitates the formation of homopolymer, which in turn hinders the movement of free radicals.

Effect of PMS

The effect of PMS on grafting parameters has been studied by varying the concentration of PMS from 5 × 10^{-3} to 21 × 10^{-3} mol dm^{-3}, and the results are presented in Figure 1. The grafting ratio, add on, efficiency, and conversion have been found to increase continuously on increasing the concentration of PMS from 5 × 10^{-3} to 21 × 10^{-3} mol dm^{-3}, whereas the homopolymer decreases. The increment in grafting
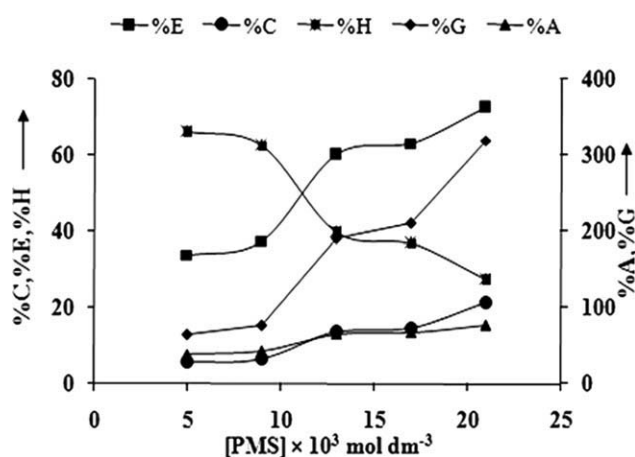
parameters might be due to the progressive reduction of PMS by TU, which produces primary free radicals[22] i.e., R$^\bullet$ = R$_1$S$^\bullet$ and SO$_4^{\bullet-}$. These primary free radicals generate more number of active sites on polymeric backbone to which monomer addition takes place.

Effect of thiourea

The variation of TU concentration from 1.6 × 10^{-3} to 4.8 × 10^{-3} mol dm^{-3} reveals that the grafting ratio, add on, conversion, and efficiency increase on increasing the TU concentration up to 3.2 × 10^{-3} mol dm^{-3} due to availability of more primary free radicals[23] (R$^\bullet$ = R$_1$S$^\bullet$ and SO$_4^{\bullet-}$), which might be formed due to the reduction of PMS by TU. However, on further increasing the concentration of TU from 3.2 × 10^{-3} to 4.8 × 10^{-3} mol dm^{-3}, the decrement in grafting parameters has been found, which is probably due to the premature termination of DMA radicals giving rise to the formation of more homopolymer. The results are given in Table II.

Effect of CmgOH

The effect of CmgOH has been observed with an aim to study the effect of its concentration (from 0.4 to 1.8 g dm^{-3}) on grafting parameters i.e., grafting ratio, add on, and efficiency. The results are presented in Figure 2. It is found that the grafting parameters increase continuously on increasing the concentration of CmgOH. This may be due to greater availability of grafting sites onto CmgOH.

Effect of H$^+$ ion

The concentration of hydrogen ion plays an important role during the reaction (Table III). The effect of hydrogen ion concentration has been studied by varying the concentration from 1.5 × 10^{-3} mol dm^{-3} to 9.5 × 10^{-3} mol dm^{-3}. It has been observed that grafting ratio, add on, conversion, and efficiency increase due to protonation of TU,[24] which takes place on increasing the hydrogen ion concentration up to 5.5 × 10^{-3} mol dm^{-3}, and the protonated species in turn react with peroxymonosulphate to give more primary free radicals.
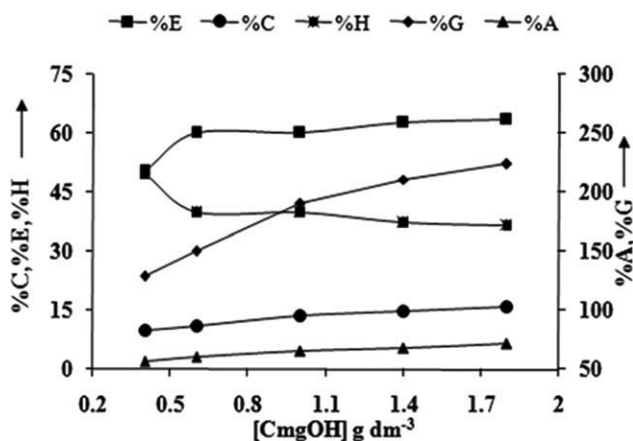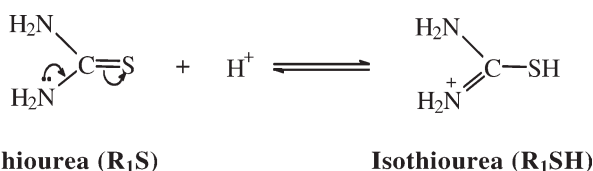

Figure 1 Effect of PMS: CmgOH = 1.0 g dm^{-3}; Time = 120 min; DMA = 16 × 10^{-2} mol dm^{-3}; TU = 3.2 × 10^{-3} mol dm^{-3}; H$^+$ = 5.5 × 10^{-3} mol dm^{-3}; Temperature = 35°C.

Figure 2 Effect of CmgOH: PMS = 13×10^{-3} mol dm^{-3}; DMA = 16×10^{-2} mol dm^{-3}; Time = 120 min; TU = 3.2×10^{-3} mol dm^{-3}; H$^+$ = 5.5×10^{-3} mol dm^{-3}; Temperature = 35°C.

Thiourea (R₁S)   **Isothiourea (R₁SH)**

However, on further increasing the concentration of [H$^+$] ions beyond 5.5×10^{-3} mol dm^{-3}, the grafting parameters decrease, whereas the homopolymer increases. It could be explained by the following reasons:

1. It is due to the premature termination of DMA radicals giving rise to the formation of homopolymer.
2. On increasing the hydrogen ion concentration, the formation of H$_2$SO$_5$ species increases due to which the concentration of HSO$_5^-$ decreases resulting in the production of less-free radical, thereby decreasing the grafting parameters.
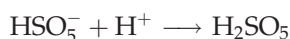
$$HSO_5^- + H^+ \longrightarrow H_2SO_5$$

TABLE III
Effect of H$^+$ Ion

H$^+$ × 10^3 (mol dm^{-3})	%G	%E	%A	%C	%H
1.5	141.5	54.2	58.6	10.2	45.8
3.5	170.0	58.7	62.9	11.9	41.3
5.5	190.3	60.2	65.6	13.7	39.9
7.5	154.5	55.8	60.7	11.2	44.2
9.5	136.9	52.3	57.8	10.2	47.8

[CmgOH] = 1.0 g dm^{-3}; [PMS] = 13×10^{-3} mol dm^{-3}; [DMA] = 16×10^{-2} mol dm^{-3}; Time = 120 mins; [TU] = 3.2×10^{-3} ml dm^{-3}; Temperature = 35°C.
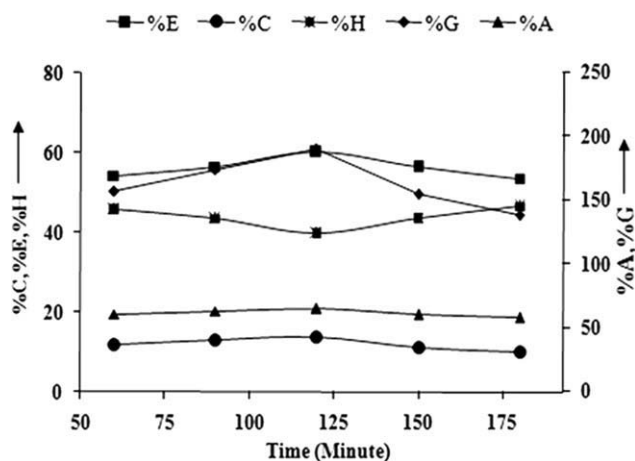
Figure 3 Effect of Time: CmgOH = 1.0 g dm^{-3}; DMA = 16×10^{-2} mol dm^{-3}; PMS = 1.3×10^{-3} mol dm^{-3}; TU = 3.2×10^{-3} mol dm^{-3}; H$^+$ = 5.5×10^{-3} mol dm^{-3}; Temperature = 35°C.

Effect of time

To investigate the effect of time on graft copolymerization, the reaction has been carried out by varying the duration of reaction from 60 to 180 min, and the results are presented in Figure 3. It has been found that the grafting ratio, add on, conversion, and efficiency increase in beginning from 60 to 120 min, and thereafter, these parameters decrease. This is attributed due to propagation of grafting chains, which takes place due to availability of more active species and this 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, and so, the grafting parameters decrease.

Effect of temperature

The results for grafting parameters at different temperatures between 25 and 45°C are summarized in Table IV. The grafting parameters increase up to 35°C and, thereafter, decrease to some extent with further increase in temperature. The increment in grafting parameters in beginning up to 35°C is

TABLE IV
Effect of Temperature

Temperature (°C)	%G	%E	%A	%C	%H
25	143.9	51.86	59.0	11.2	48.1
30	160.2	54.2	61.6	12.3	45.8
35	190.3	60.2	65.6	13.7	39.9
40	154.9	56.4	60.8	11.0	43.6
45	140.5	53.7	58.4	10.2	46.4

[CmgOH] = 1.0 g dm^{-3}; [PMS] = 13×10^{-3} mol dm^{-3}; Time = 120 mins; [TU] = 3.2×10^{-3} mol dm^{-3}; [H$^+$] = 5.5×10^{-3} mol dm^{-3}; [DMA] = 16×10^{-2} mol dm^{-3}.
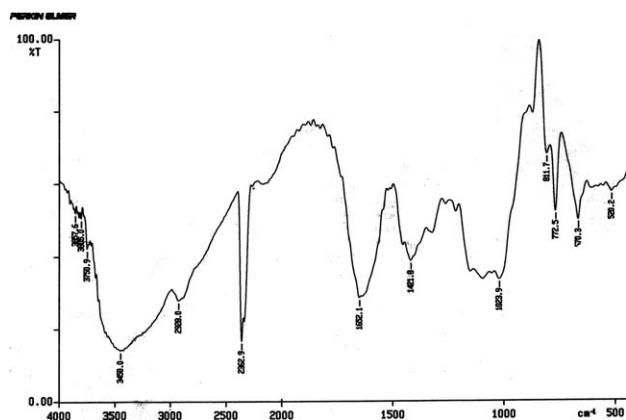
Figure 4 IR spectrum of partially carboxymethylated guar gum.

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 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 PMS into HSO_4^-, H_2O, and O_2. Because O_2 acts as a scavenger for free radicals, which reacts with primary free radicals, thereby lowering the free radical concentration.

IR spectra of partially carboxymethylated guar gum and graft copolymer

IR spectrum of CmgOH (Fig. 4) shows characteristic absorption bands arising from O—H stretching (broad) and C—O stretching near 3450.0 cm^{-1} and 1023.9 cm^{-1}, respectively. On comparing the spectra of both, CmgOH and its graft copolymer, CmgOH-g-DMA (Fig. 5) shows a sharp band at same wave
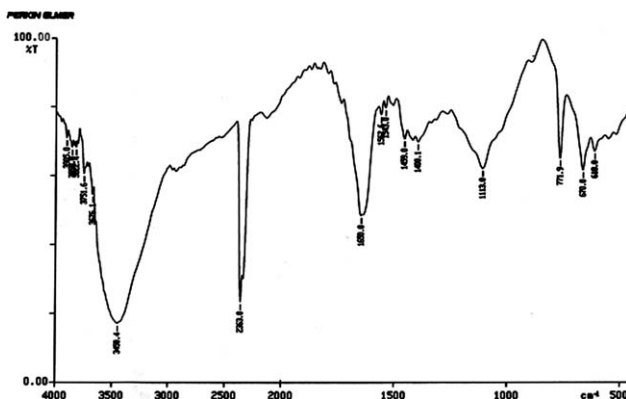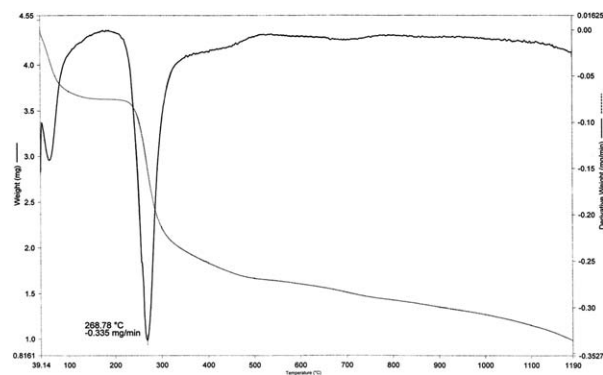

Figure 6 Thermogravimetric trace of partially carboxymethylated guar gum.

number i.e., 3450.0 cm^{-1}, and a peak present at 1023.0 cm^{-1} in the spectrum of pure carboxymethylated guar gum disappeared from the spectrum of graft copolymer. Both, the sharpness of band and disappearance of peak, indicate the participation of hydroxyl groups in chemical reaction. The attachment of DMA is also further confirmed by the appearance of additional characteristic absorption bands at 1650.0 and 1400.0 cm^{-1} due to C=O stretching vibration and C—N stretching vibration of tertiary amide of DMA, respectively. The presence of additional peaks/bands in the spectrum of CmgOH-g-DMA also shows that grafting might have been taken place on —OH sites of backbone.

Thermogravimetric analysis

Thermogravimetric curve of CmgOH (Fig. 6) shows single step degradation. The weight loss 1.5% is due to loss absorbed volatile methanol at 54.9°C. The polymer decomposition temperature[25] has been found nearly at 250.0°C. The weight loss increases with increase in temperature from 260.9 to 275.2°C and thereafter decreases and attains maximum at 284.2°C. The integral procedural decomposition temperature (IPDT) is 189.5°C. T_{max}, the temperature at
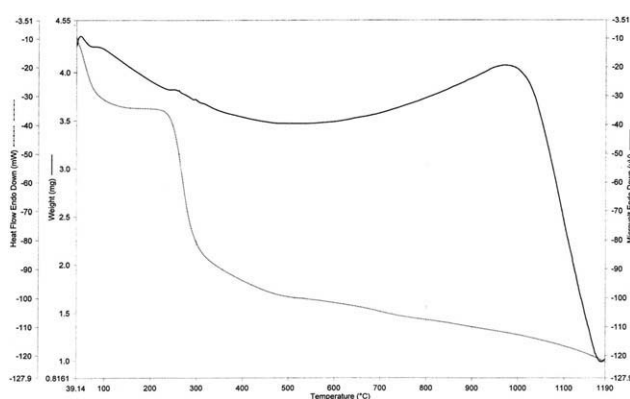

Figure 5 IR spectrum of partially carboxymethylated guar gum-g-N,N'-dimethylacrylamide.

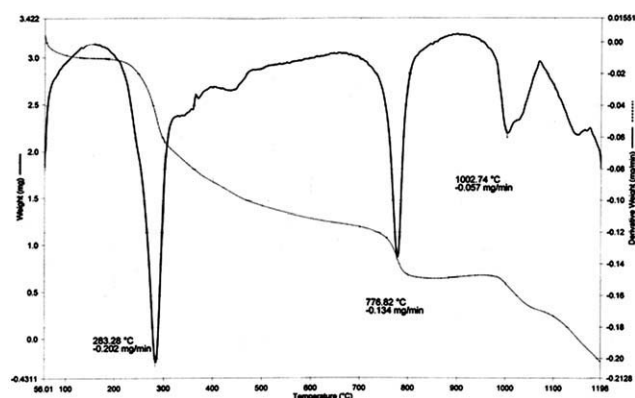**Figure 7** Differential thermal trace of partially carboxymethylated guar gum.

Figure 8 Thermogravimetric trace of partially carboxymethylated guar gum-g-N,N'-dimethylacrylamide.

which maximum degradation occurred, is 268°C, and final decomposition temperature (FDT) has been observed at about 900°C. The differential trace of CmgOH is shown in the form of Figure 7. CmgOH-g-DMA 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 thereafter decreases and attains maximum at 283.3°C. Thermogravimetric curve of CmgOH-g-DMA (Fig. 8) shows three step degradations. First T_{max} 283.3°C is due to the elimination of $-CH_3$ groups, which is also confirmed by a peak appeared in DTA curve of CmgOH at near 300°C (Fig. 9). The second T_{max} 776.8°C is due to the elimination of N_2 group, confirmed by a peak appeared at about 800°C in DTA curve, and the third T_{max} at 1002.7°C is due to the elimination of CO_2 molecule from pendent chains attached to the CmgOH. The IPDT and FDT have been found at about 347.8°C and 1150°C. On comparing the thermal analysis of parent backbone of CmgOH and graft copolymer (CmgOH-g-DMA), it has been observed that final and integral procedural decomposition have been found to be higher for graft copolymer. The higher values of FDT and IPDT indicate thermal stability toward the graft copolymer of
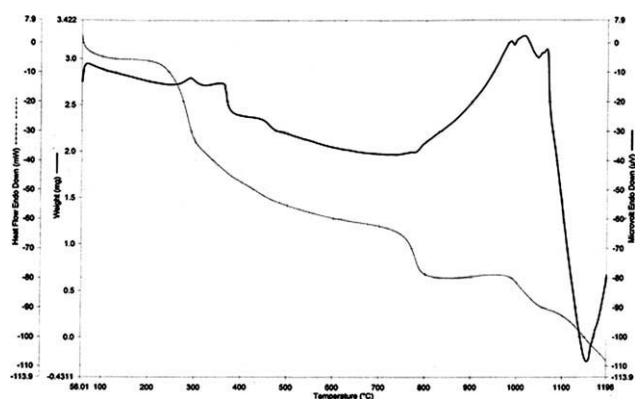
TABLE V
Data of Thermogravimetric Analysis

Sample code	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
C (CmgOH)	250.0	900	268	189.5
C_N (%G = 190.3)	110.5	1150	283.3, 776.8, 1002.7	347.8

CmgOH-g-DMA. The data of thermogravimetric analysis are also presented in Table V.

Study of the properties

Swelling test

An increase in the weight of graft copolymer has been recorded by performing swelling test. The results have been summarized in Table VI, which indicates that swelling ratio and swelling percent depend on the concentration of monomer used while grafting. As DMA is a hydrophilic monomer, it increases the water retention character of graft copolymer. On increasing the concentration of DMA, grafting is increased, which may result into coiling network of poly(DMA), 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 DMA concentration pendant chain of poly(DMA) grows thereby increasing the swelling capacity of graft copolymer.

Flocculating properties

Plots of supernatant turbidity versus polymer dosage for coking and noncoking coals are given in Figure 10. It has been found that grafted copolymer (CmgOH-g-DMA) gives better performance by showing lower turbidity than CmgOH itself. This phenomenon could be explained by considering bridging mechanism.[26,27] In grafted copolymer, the dangling of

Figure 9 Differential thermal trace of partially carboxymethylated guar gum-g-N,N'-dimethylacrylamide.

TABLE VI
Swelling Capacity of Partially Carboxymethylated Guar Gum-g-N,N'-Dimethylacrylamide

Sample code	DMA × 10^{-2} (mol dm^{-3})	%G	P_S	S_R
C_{N1}	8	144.7	112.4	1.124
C_{N2}	12	157.6	125.0	1.250
C_{N3}	16	190.3	156.7	1.567
C_{N4}	20	164.5	151.9	1.519
C_{N5}	24	137.1	140.0	1.400

[CmgOH] = 1.0 g dm^{-3}; [PMS] = 13 × 10^{-3} mol dm^{-3}; Time = 120 mins; [TU] = 3.2 × 10^{-3} mol dm^{-3}; [H$^+$] = 5.5 × 10^{-3} mol dm^{-3}; Temperature = 35°C; CN indicates the sample of graft copoymer (partially carboxymethylated guar gum-g-N,N'-dimethylacrylamide).
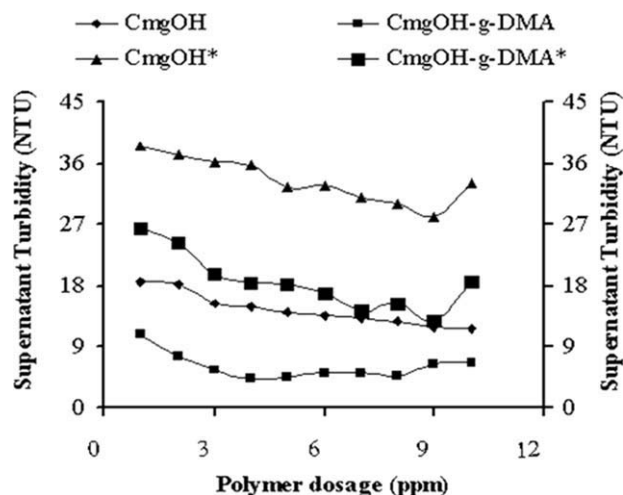
Figure 10 Effect of polymer dosage on turbidity for coking coal and noncoking coal*.

poly(DMA) chains have better approachability[28] to the contaminant coal particles, and hence, increases its flocculation capability.[29] The difference in turbidity value in coking coal and noncoking coal in coal suspension is due to difference in negative charge density, which is higher in noncoking coal in aqueous solution.[30] Thus, by grafting of poly(DMA) onto CmgOH, efficient flocculants have been obtained, and it could be used for the treatment of coal waste water.

CONCLUSIONS

The thermal data show that the synthesized graft copolymer is thermally more stable than pure CmgOH. The synthesized graft copolymer i.e., CmgOH-*g*-DMA shows better results for swelling and flocculating properties in comparison with CmgOH and thus could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of DMA 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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