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Synthesis and characterization of a novel graft copolymer of partially carboxymethylated guar gum and N-vinylformamide

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ABSTRACT

Graft copolymer of partially carboxymethylated guar gum (CMGOH) and N-vinylformamide (NVF) was synthesized by free radical polymerization using 2,2-Azobis [2-(2-imadazolin-2-yl) propane] dihydrochloride (AIPH) as initiator. The effect of various reaction parameters such as concentration of NVF, CMGOH, sulphuric acid and AIPH, as well as reaction time and temperature were investigated, and the grafting conditions were optimized. Percent total conversion, % grafting, grafting efficiency (%) and percent add on under different conditions were evaluated and compared. The reaction mechanism for graft copolymerization discussed. Studies on swelling, metal ion uptake and flocculation properties were carried out in aqueous medium and the results obtained are presented and discussed. Both CMGOH and its corresponding graft copolymer samples were characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis. Looking at the reasonable results obtained, the synthesized graft copolymers CMGOH-g-NVF, may be exploited as potential candidates for some industrial important applications as flocculent superabsorbent, and other similar applications.

1. Introduction

Over the past two decades, a great deal of research has been carried out to produce a variety of advanced and hybrid polymeric materials (Liu et al., 2009; Yu, Dean, & Li, 2006) for various industrial applications. Graft copolymers derived from natural and synthetic materials are gaining large importance in recent years as they may be employed in diverse applications including cosmetics, biomedicine, pharmaceutical applications and biotechnology (Baron, Rodriguez-Hernandez, Ibarboure, Derail, & Papon, 2009; Guan, Luo, Qiu, & Tang, 2010; Mostafa, Abdul Rahim Samarkandy, & El-Sanabary, 2011; Xun et al., 2011). Graft copolymers are a special type of copolymer in which the side chains are structurally distinct from the main chain. Considerable work has been done on graft copolymerization of different monomers on polymeric backbones. In this paper, an attempt is made to synthesize a hitherto unreported graft copolymer of partially carboxymethylated guar gum (CMGOH) and N-vinylformamide (NVF) by free radical polymerization using 2,2-Azobis [2-(2-imadazolin-2-yl) propane] dihydrochloride (AIPH) as initiator. Among other approaches, free radical polymerization method, used in this study, was observed to be suitable for modifying the natural polymers mostly polysaccharides (Cardona & George, 2002; Dargaville, George, Hill, & Whittaker, 2003; Egboh, George, & Barrie, 1984; Fikentscher & Kröner, 1992; Madl & Spange, 2000; Spange, Madl, Eismann, & Utecht, 1997). In recent past, different graft copolymers were prepared by adding the new properties of synthetic monomers to the natural polymers with minimum loss of native properties (Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Shrivastava, Mishra, & Behari, 2008; Mishra, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, & Behari, 2010; Tripathy, Mishra, & Behari, 2009; Tripathy, Mishra, Yadav, & Behari, 2010; Yadav et al., 2012); the method also has industrial significance (Misra & Bajpai, 1982; Misra & Bhasilal, 1978; Sarac, 1999; Guo, Skinner, Harcum, & Barnum, 1998). Partially carboxymethylated guar gum is a derivative of naturally occurring guar gum (Thaker & Trivedi, 2005) which is basically composed of a straight chain of D-mannose units, joined by β(1–4) glycoside linkages, and bearing a single D-galactose unit on approximately every alternate D-mannose. The versatile polymer is used as a vehicle for oral controlled release applications due to its low price and other properties (Guo, Skinner, Harcum, & Barnum, 1998). Guar gum and its derivative are also used in other applications such as in oil industry as drilling muds and fingering fluids in enhanced oil recovery while in textile industry, they facilitate improved printing (Turk & Schneider, 2000). Although, guar gum and their derivatives enjoy a wide range of applications, they are highly susceptible to microbial attack (Srivastava,

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Tripathy, Mishra, & Behari, 2007). Even though many investigations were carried out to prepare biomaterials from CMGOH for numerous other applications but reports on grafting onto the partially carboxymethylated guar gum are scanty (Tripathy, Mishra, Srivastava, Mishra, & Behari, 2008; Yadav, Sand, Mishra, & Behari, 2010). In view of this, a graft copolymer of partially carboxymethylated guar gum using a new monomer of N-vinylformamide (NVF) is prepared to explore flocculation and super absorption properties. NVF is a key monomer used in the synthesis of linear cationic polymers as well as several other derivatives in preparative synthetic chemistry (Kröner, Dupuis, & Winter, 2000). Poly(NVF) can easily be converted to poly(N-vinyl amine) by hydrolysis in either acidic or basic aqueous solutions (Gu, Zhu, & Hrymak, 2002; Yamamoto et al., 2003). Poly(NVF) and their derivatives are employed in applications such as papermaking (Wang, Kitaoka, & Tanaka, 2003), flocculants (Burkert et al., 1984), adhesives (Sommese & Furman, 1994), oil & gas recovery (Pinschmidt & Lai, 1990) and many others (Stach et al., 2010). Encouraged by the applications of partially carboxymethylated guar gum and N-vinyl formamide, a novel graft copolymer of partially carboxymethylated guar gum and N-vinyl formamide, i.e. CMGOH-g-NVF, is synthesized using 2,2-Azobis [2-(2-imadazolin-2-yl)propane] dihydrochloride (AIPH). Partially carboxymethylated guar gum [degree of substitution (DS) = 0.291] is chosen as substrate polymeric backbone in this study. The various graft copolymers synthesized are used to examine swelling, metal ion uptake and flocculation properties, and the results obtained are presented and discussed.

2. Experimental

2.1. Materials

NVF procured from (Sigma–Aldrich, U.K.) was used after distillation under reduced pressure (14 mm Hg at 55 °C, under nitrogen atmosphere). Both AIPH and CMGOH received as gift samples from Wako chemical, Japan and Hindustan Gums, Ltd., India, respectively, were used. Sulphuric acid and Methanol (E-Merck, India) were used to maintain hydrogen ion (H^+) concentration and as solvent for precipitation, respectively. The other reagents used were of analytical grade. Triple distilled water was used to prepare all aqueous solutions. Coking and non-coking coal powders as received from Bokaro steel plant, Bokaro were used for flocculation studies.

2.2. Graft copolymerization

Graft copolymerization of NVF onto CMGOH was carried out using free radical polymerization using AIPH. Various amounts of monomer NVF, sulphuric acid and CMGOH were employed at different temperature and reaction time to optimize the grafting conditions. A calculated amount of NVF and sulphuric acid solutions were added simultaneously into the glass reactor. A slow stream of oxygen free nitrogen gas was purged for 30 min. A known amount of AIPH solution was added to initiate the reaction. The reaction was performed under nitrogen atmosphere at constant temperature. After desired time period, the reaction was quenched by letting air into reactor. The grafted copolymer was precipitated by pouring the reaction mixture into water–methanol mixture (1:4) and then filtered. The precipitate was dried thoroughly and weighed. The poly(NVF) formed was remained in the filtrate.

2.3. Separation of homopolymer

A pinch of hydroquinone was added to the filtrate to avoid additional homo polymerization and it was concentrated by distillation under reduce pressure. The concentrated filtrate was poured into excess amount of pure methanol to precipitate the homopolymer of NVF. Poly(NVF) thus obtained was filtered, dried and weighed.

2.4. Characterization

2.4.1. FTIR spectroscopy

The samples of neat CMGOH and graft copolymers were analyzed using JASCO FT/IR model and the spectra recorded in the range 500–4000 cm^{-1}.

2.4.2. Thermal analysis

The thermal analysis of CMGOH and CMGOH-g-NVF were carried in an inert atmosphere at heating rate of 15 °C per minute in temperature range of ambient to 1400 °C using NETZSCH-STA 409C/CD thermal analyzer.

2.5. Evaluation of graft copolymers

2.5.1. Swelling

For swelling study, 0.05 g of graft copolymer sample was immersed in 20 ml of triple distilled water and kept undisturbed for 24 h at ambient temperature until the equilibrium swelling was reached. The graft copolymer samples, used in this study, were synthesized by varying the concentration of NVF from 8×10^{-2} mol dm^{-3} to 24×10^{-2} mol dm^{-3}. After complete swelling, the water from the surface of swollen graft copolymer was removed by pressing it between two folds of filter paper, and then weight of swollen graft copolymer was taken. The percent swelling (P_S) was calculated by using the following expression (Abd EL-Rehim, Hegazy, & Ali, 2000; Bajpai, Bajpai, & Shukla, 2001; Bajpai, Shukla, Bhanu, & Kankane, 2008):

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

2.5.2. Metal ion uptake

Three metal ion Pb^{2+}, Ni^{2+} and Zn^{2+} solutions (standard concentration) were prepared. For metal ion uptake study, 0.02 g of graft copolymer was immersed in 10 ml of their respective metal ion solutions and kept for 24 h. The graft copolymer samples of different compositions, used in this study, were synthesized by varying the concentration of NVF from 8×10^{-2} to 24×10^{-2} mol dm^{-3}. The strength of unabsorbed metal ion solution was determined by standard method (Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Shrivastava, et al., 2008). All sorption parameters were calculated by using following equations (Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Shrivastava, et al., 2008; Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

$$\text{Percent uptake}\,(P_u) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion in feed}} \times 100$$

$$\text{Partition coefficient}\,(K_d) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion left in solution}} \times \frac{\text{Vol. of solution (ml)}}{\text{Wt. of dry polymer (g)}}$$

$$\text{Retention capacity}\,(Q_r) = \frac{\text{Amount of metal ion in polymer (mEquiv.)}}{\text{Wt. of dry polymer (g)}}$$

2.5.3. Flocculation

In 1.0 l beaker, 200 ml of 1% wt coal suspension was taken. The beaker was placed in flocculation unit with the stirrer blade dipping in the suspension. Under a low stirring condition, required quantity of polymer solution was added to make predetermined dose with respect to suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 5 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 (supplied by ISO-TECH SYSTEM, Varanasi) to express the turbidity in nephelometric unit (N.T.U.).

3. Results and discussion

3.1. Fanta's equation

The grafting parameters were calculated according to Fanta's (Fanta, 1973) equation. The percent grafting ratio (%G) is calculated as the ratio of the weight of the grafted polymer to the weight of the substrate (CMGOH) multiplied by 100:

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

The percent add on is taken as the ratio of the weight of the grafted polymer (synthetic polymer) to the weight of graft copolymer.

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

The percent conversion is taken as the ratio of the weight of the grafted polymer to the weight of the monomer (monomer charged).

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

The percent efficiency is taken as the ratio of the weight of the grafted polymer to the total weight of grafted polymer and homopolymer.

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

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

3.2. Optimization of reaction conditions

The effect of various reaction parameters such as concentration of NVF, CMGOH, sulphuric acid and AIPH, as well as reaction time and temperature were investigated, and the grafting conditions were optimized. The effect of different reaction conditions on grafting parameters is presented and discussed below.

3.2.1. Effect of 2,2-Azobis [2-(2-imadazolin-2-yl) propane] dihydrochloride (AIPH) concentration

The effect of free radical initiator on grafting reaction was studied by varying the concentration of AIPH from 1.24×10^{-3} to 3.72×10^{-3} mol dm^{-3} and the results are displayed in Fig. 1a. It is observed that the values of grafting ratio, add on and efficiency increased up to a certain limit 102.3%, 83.1% and 50.6%, respectively, with a reverse trend in conversion. It is noticed that the monomer conversion (%C = 26.3%) was high because of higher homo polymer formation (%H = 73.2%). The increase in grafting ratio, add on and efficiency is attributed to the formation of more primary free radicals which can attack on active sites on backbone of CMGOH. On further increasing the concentration from 2.48×10^{-3} to 3.72×10^{-3} mol dm^{-3}, the grafting parameters (grafting ratio, add on and efficiency) decreased due to unavailability of more active sites on backbone (CMGOH) whereas formation of homo polymer of NVF increased from 16.9 to 47.6% due to termination of monomer macro radicals.

3.2.2. Effect of N-vinylformamide (NVF) concentration

The effect of N-vinylformamide (NVF) on the grafting parameters was studied by varying the concentration of N-vinylformamide (NVF) from 8×10^{-2} mol dm^{-3} to 24×10^{-2} mol dm^{-3}, and the results are presented in Fig. 1b. It is observed that the values of grafting ratio, efficiency, add on and conversion increase up to a definite value 102.3%, 83.1% and 50.6% and 10.8%, respectively. In the concentration range (from 8×10^{-2} mol dm^{-3} to 16×10^{-2} mol dm^{-3}), formation of homo polymer decreases considerably (from 43.0% to 16.9%). The improvement in grafting parameters is probably due to increased availability NVF to partially carboxymethylated guar gum macro radicals and absence of homopolymer. Further, increasing the concentration of monomer NVF from 16×10^{-2} to 24×10^{-2} mol dm^{-3}, leads to more formation of homo polymer NVF (16.9–36.0%) due to termination of monomer macro radicals. In turn, the grafting ratio, efficiency, add on and conversion decreased to lower values (77.6%, 64.0% and 43.7%, and 7.1%, respectively). It may be due to increased homo polymer formed prevents the mode of monomer molecules to partially carboxymethylated guar gum macro radicals (Sand, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, Tripathy, & Behari, 2011).

3.2.3. Effect of partially carboxymethylated guar gum (CMGOH) concentration

The effect of partially carboxymethylated guar gum (CMGOH) on grafting parameters was studied by varying the concentration of partially carboxymethylated guar gum from 0.6 to 1.4 g dm^{-3} and results are presented in Fig. 1c. It is seen that the values of grafting ratio (25.3–122.1%), efficiency (22.6–97.8%), add on (20.2–54.9%) and conversion from 9.8% to 10.9%, increased continuously through out on increasing the concentration of partially carboxymethylated guar gum from 0.6 to 1.4 g dm^{-3}. Higher values are due to the availability of more grafting active sites on the partially carboxymethylated guar gum. The homopolymer formation decreased (from 77.3% to 2.2%) due to high viscosity of partially carboxymethylated guar gum (CMGOH) which hinders the movement of monomer molecules (Mishra, Sand, Mishra, Yadav, & Behari, 2010).

3.2.4. Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the reactions were carried out at various concentrations of sulphuric acid from 1×10^{-3} to 3×10^{-3} mol dm^{-3} and results are presented in Fig. 1d. It is observed that the values of grafting ratio, efficiency, add on and conversion increased up to a certain limit 102.3%, 83.1% and 50.6% and 10.8%, respectively, in the range from 1×10^{-3} to 2×10^{-3} mol dm^{-3} and this increase is due to the formation of protonated species. These species react with NVF (Behari, Banerjee, Srivastava, & Mishra, 2005) to form macroradicals of NVF which consequently attack on active sites of CMGOH. These monomer macro radicals are responsible for propagation of further growing grafted chains. However, further increase beyond 2×10^{-3} mol dm^{-3}, these parameters decrease may be due to premature termination of NVF and CMGOH (Hakon, 1955).

3.2.5. Effect of reaction time

The effect of reaction time on grafting parameters was investigated by varying the reaction periods from 60 to 180 min. The results are summarized in Table 1. It is observed from the table that the values of grafting ratio, efficiency, add on and conversion

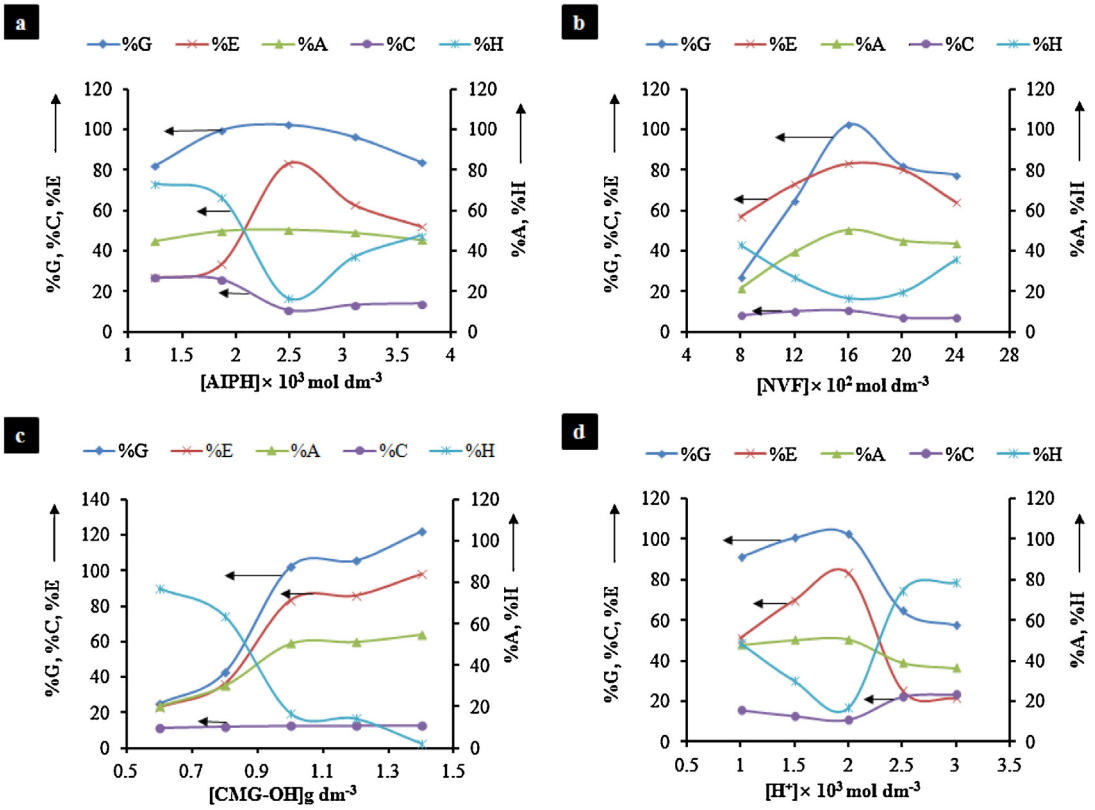


Fig. 1. Effect of AIPH concentration (a), NVF concentration (b), CMGOH concentration (c) and hydrogen ion concentration (d) on grafting parameters.

increased up to certain optimum values 102.3%, 83.1% and 50.6% and 10.8%, respectively, in the range from 60 to 120 min. However, further increase beyond 120 min these parameters decreased. On increasing the reaction time, the propagation of grafting chains takes at faster rate due to availability of more active sites, which accounts for higher grafting (Sand, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, Tripathy, et al., 2011). On further increasing time interval (in the range of 120–180 min), the mutual annihilation of growing chains might occur which leads to lower values (Sand, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, Tripathy, et al., 2011).

3.2.6. *Effect of reaction temperature*

The effect of temperature on grafting parameters was examined at different temperatures from 35 °C to 55 °C and the results are summarized in Table 1. It is seen that, in the temperature range from 35 °C to 45 °C, values of grafting ratio, efficiency and add on increased whereas the conversion values decreased. This increase is due to increased rate of production of primary free radicals, which generate more number of grafting sites. However, at higher temperature beyond 45 °C, the grafting parameters decrease due to the premature termination of growing graft chain (Yadav, Mishra, Sand, & Behari, 2011).

3.3. *Mechanism*

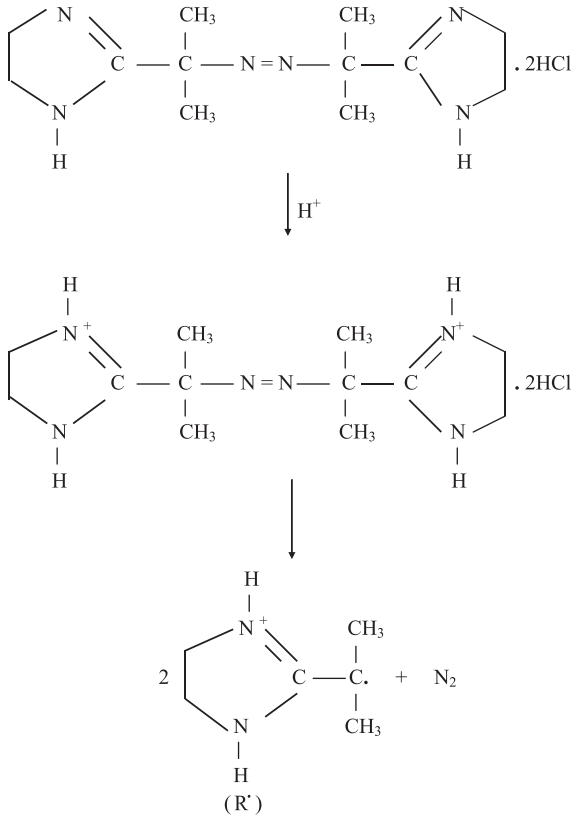
On the basis of experimental results, the following provisional mechanism is proposed for graft copolymerization of N-vinylformamide (NVF) onto partially carboxymethylated guar gum using 2,2-Azobis [2-(2-imadazolin-2-yl) propane] dihydrochloride as a free radical initiator. It is assumed that in presence of hydrogen ion, the initiator gets protonated and subsequent

Table 1
Effect of reaction time and temperature on grafting parameters.

Time[a] (min)	Variation										
	%G	*%E*	*%A*	*%C*	*%H*	Temp.[b] (°C)	*%G*	*%E*	*%A*	*%C*	*%H*
60	68.3	41.1	40.5	14.5	58.8	35	75.3	36.1	42.9	18.3	63.8
90	82.8	57.6	45.3	12.6	42.7	30	81.9	51.4	45.0	14.0	48.5
120	102.2	83.1	50.5	10.8	16.8	45	102.2	83.1	50.5	10.8	16.8
150	81.2	54.3	44.8	13.1	45.6	50	82.9	51.7	45.3	14.0	48.2
180	71.3	40.6	41.6	15.4	59.3	55	80.4	48.8	44.5	14.4	51.1

[a] [NVF] = 16×10^{-2} mol dm^{-3}, [AIPH] = 2.48×10^{-3} mol dm^{-3}, [CMGOH] = 1.0 g dm^{-3}. [H^+] = 2×10^{-3} mol dm^{-3}, Temp. = 45 °C.
[b] [NVF] = 16×10^{-2} mol dm^{-3}, [AIPH] = 2.48×10^{-3} mol dm^{-3}, [CMGOH] = 1.0 g dm^{-3}. [H^+] = 2×10^{-3} mol dm^{-3}, Time = 120 min.

homolytic fission of the bond, leads to the formation of free radical as follows.



The R• radicals abstract hydrogen atom from partially carboxymethylated guar gum (CMGOH) molecule producing a macro radical (CMGO•) as shown below, since initiation of vinyl polymerization is faster than H-abstraction by primary radicals. After the chain propagation, the grafted chains are terminated by coupling mechanism. The details of the mechanism are given below:

Initiation

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

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

where CMGOH = partially carboxymethylated guar gum, M = Monomer, CMGO• = Macro radical

Propagation

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

$CMGOM^{\bullet} + M \rightarrow CMGOM_1{}^{\bullet}$

. . . . . .

$CMGOM_{n-1}{}^{\bullet} + M \rightarrow CMGOM_n{}^{\bullet}$

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

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

. . . . . .

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

Termination

$$CMGOM_n^{\bullet} + CMGOM_m^{\bullet} \rightarrow \text{Graft copolymer}$$

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

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

3.4. Characterization of graft copolymer

3.4.1. FTIR spectroscopy

The IR spectrum of the graft copolymer is given in Fig. 2. It is clearly seen that a broad band at 3415.7 cm^{-1}, which is a typical of hydrogen bonded O—H stretch from alcoholic and bound water. The same absorption band appeared at 3450.0 cm^{-1} in the spectrum of partially carboxymethylated guar gum (Sand, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, Tripathy, et al., 2011; Tripathy et al., 2008). On comparing the two IR spectra (CMGOH and CMGOH-g-NVF) (Fig. 2), it is observed that there is variation in intensity of OH stretching vibration and shifting of the peak from 3450.0 cm^{-1} to 3415.7 cm^{-1}, indicating the participation of hydroxyl groups in the grafting reaction. The grafting of monomer is further confirmed by a characteristic absorption band present at 3781.8 cm^{-1} due to —N—H stretching vibration (amide II) of pendant N-vinylformamide chain. The band present at 1121.5 cm^{-1} is attributed to —CN stretching vibration of secondary amide.

Table 2
Swelling.

Sample[a]	[NVF] × 10^2 mol dm^{-3}	%G	(Ps)
A	8	27.1	764.3
B	12	64.7	964.1
C	16	102.2	1503.1
D	20	82.2	1220.8
E	24	77.6	1054.9

[a] Graft copolymers (A, B, C, D, and E) synthesized at different concentrations of NVF.

3.4.2. Thermal analysis

The thermal stability of the graft copolymer is examined by the TGA and DSC analysis and the respective thermograms are shown in Figs. 3 and 4, respectively. The TGA curve of partially carboxymethylated guar gum (Sand, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, Tripathy, et al., 2011; Tripathy et al., 2008) shows single step degradation. There is almost no weight loss till 50 °C, whereas a slight decomposition begins beyond 50 °C (weight loss 1.5% at 55 °C) which could be assigned due to methanol in the graft copolymer. However, the polymer decomposition temperature is observed at 250 °C. The weight loss increases with increasing temperature from 260 °C to 275 °C and attains maximum T_{max}, at 269 °C and the final decomposition temperature (FDT) is observed at about 900 °C. The thermal stability of CMGOH and CMGOH-g-NVF was determined by calculating IPDT values using following equation:

$$T_A^* = (T_{end} - T_{initial})A^* + T_{initial}$$

as per the procedure given in Doyle (1961). The following IPDT values 189 °C (CMGOH) and 225 °C (CMGOH-g-NVF) are obtained. The degradation of the graft copolymer takes place in two steps, the first between 200 and 300 °C and the second from 350 to 450 °C (Fig. 3) and in accordance, two maximum temperatures (T_{max}) are observed at about 273 °C and 417 °C (Scheme 1). The first, T_{max} is due to the elimination of —CO_2 from the polymeric backbone, which is also confirmed by the presence of exothermic peak in DTA curve (241 °C). The second loss at 417 °C may be due to the elimination of —CO from pendent chain attached to the polymeric back bone, which is also confirmed by the presence of exothermic peak in DTA curve (494 °C) as shown in Fig. 4. The final decomposition temperature (FDT) was found at 1150 °C. The higher values of FDT, IPDT, and the exclusive two steps degradation process indicate that the graft copolymer (CMGOH-g-NVF) is more stable than the substrate polymer backbone (CMGOH).

3.5. Properties of graft copolymer

3.5.1. Swelling

The equilibrium swelling data are shown in Table 2 and in accordance the percent swelling increases with increasing grafting ratio. This behaviour may be interpreted due to hydrophilic

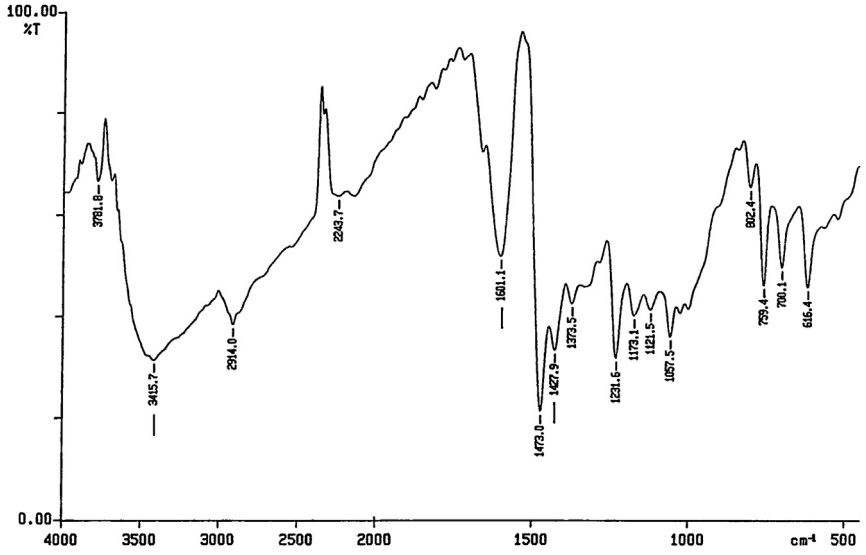


Fig. 2. IR spectrum of graft copolymer (CMGOH-g-NVF).

nature of monomer attached to the polymeric backbone of partially carboxymethylated guar gum. Thus the percentage of hydrophilic character in graft copolymer increases with increasing chain of pendent poly(N-vinylformamide) onto partially carboxymethylated guar gum thereby increasing swelling capability of graft copolymer (Sand, Yadav, Mishra, & Behari, 2011; Sand, Yadav, Mishra, Tripathy, et al., 2011; Tripathy et al., 2008).

3.5.2. Metal ion uptake

The results of sorption behaviour of substrate and graft copolymer which are determined in terms of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) are given in Table 3. It is noticed that the values of (P_u), (K_d) and (Q_r) increase directly with increasing percent grafting and is endorsed due to increased pendent chains of poly(N-vinylformamide). The results also indicate that lower values of metal ion uptake by Zn^{2+} compared to two other metal ions used.

3.5.3. Flocculation

The coal powder is uniformly suspended in the beaker which is placed in the flocculation unit with the stirrer dipping in the suspension and it is stirred. The turbidity values of supernatant liquids are taken as the measurement of flocculation efficiency of partially carboxymethylated guar gum and its corresponding graft copolymer. Plots of turbidity values versus flocculent dosage for coking and non-coking coals are given in Fig. 5. It is clearly seen from the figure that the performance of graft copolymer CMGOH-g-NVF is better than pure CMGOH. This is mainly due to the better approachability of the dangling of poly(N-vinylformamide) chains to the contaminant coal particles, which easily form bigger flocs due to bridging mechanism and settle down at the bottom (Bratby, 1980;

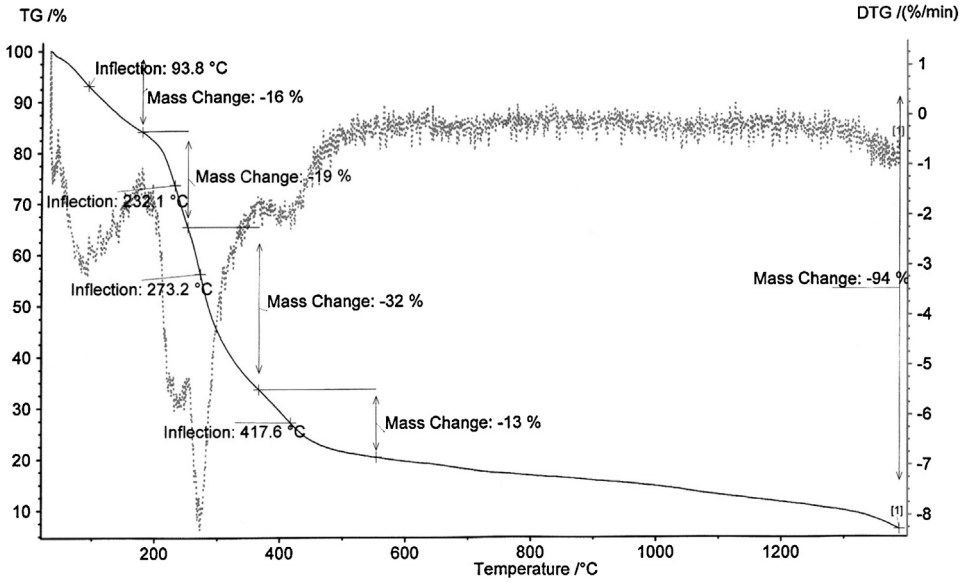


Fig. 3. Thermogravimetric analysis of graft copolymer (CMGOH-g-NVF).

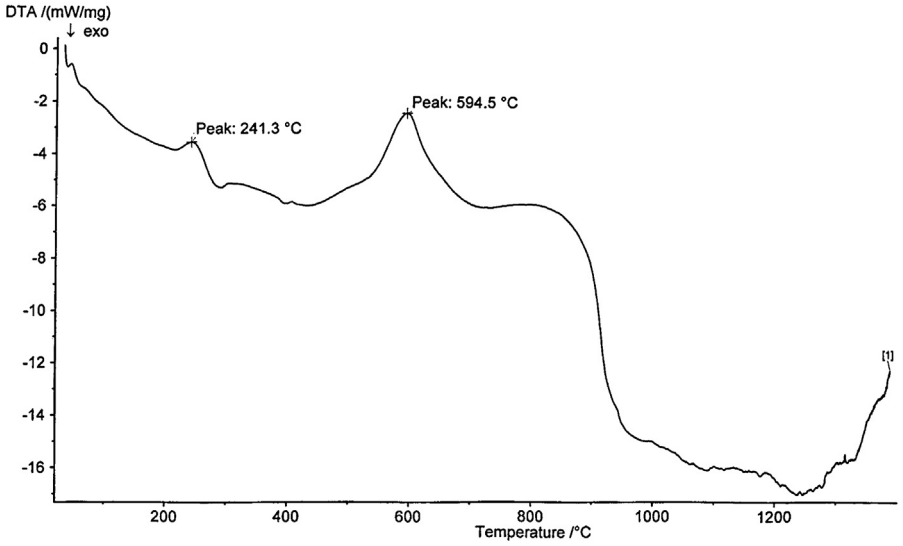
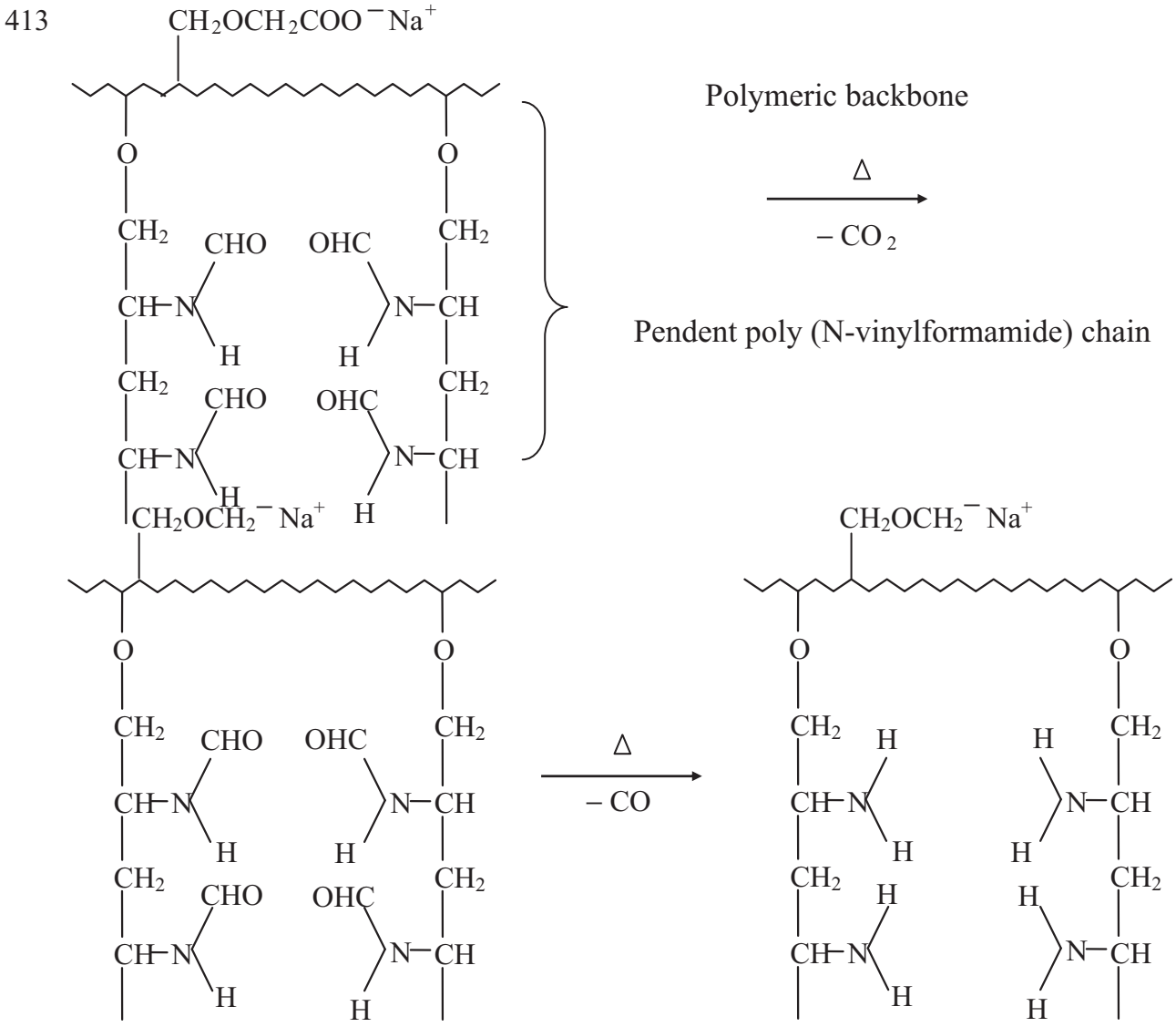


Fig. 4. Differential thermal analysis of graft copolymer (CMGOH-g-NVF).



Scheme 1. Representation of degradation steps of graft copolymer.

Table 3
Metal ion uptake.

Sample[a]	[NVF] × 10^2 mol dm^{-3}	%G	Pb^{2+} sorption			Ni^{2+} sorption			Zn^{2+} sorption		
			P_u	K_d	Q_r	P_u	K_d	Q_r	P_u	K_d	Q_r
CMGOH	–	–	2.0	5.3	0.5	1.0	2.6	0.2	0.9	2.3	0.2
A	8	27.1	5.2	13.7	1.2	4.2	11.1	1.0	3.7	9.8	1.0
B	12	64.7	7.2	19.6	1.7	6.3	17.0	1.5	4.7	12.3	1.2
C	16	102.2	13.5	39.1	3.2	12.7	36.5	3.0	9.4	26.0	2.5
D	20	82.2	11.4	32.3	2.7	10.6	29.7	2.5	8.4	23.1	2.2
E	24	77.6	9.3	25.8	2.2	8.5	23.2	2.0	6.6	17.6	1.7

[a] Graft copolymers (A, B, C, D, and E) synthesized at different concentrations of NVF.

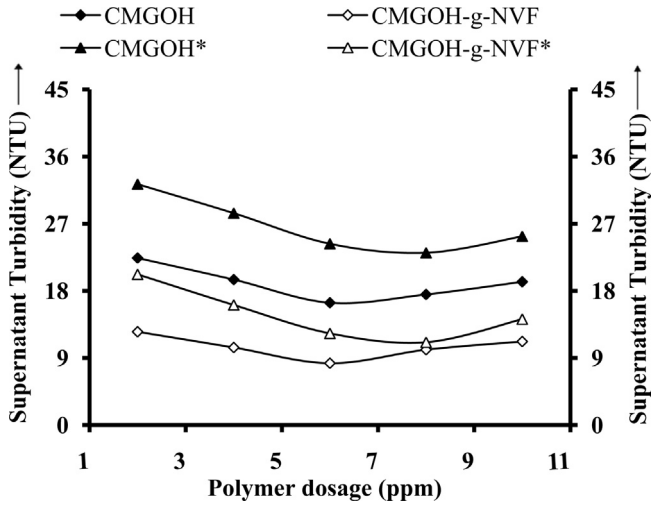


Fig. 5. Effect of polymer dosage on turbidity for coking coal and non-coking coal*.

Gregory, 1982; Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Shrivastava, et al., 2008; Tripathy et al., 2009).

4. Conclusions

A novel graft copolymer of partially carboxymethylated guar gum and N-vinylformamide CMGOH-g-NVF, is successfully synthesized by free radical polymerization using 2,2-Azobis[2-(2-imadazolin-2-yl)propane] dihydrochloride as initiator. The evidence of grafting of N-vinylformamide through hydroxyl group of CMGOH is shown by the FTIR spectral data. The thermal analysis data (TGA and DSC) reveal that graft copolymer CMGOH-g-NVF is more stable than pure CMGOH. The graft copolymers synthesized with varying concentration of N-vinylformamide show enhanced swelling behaviour, metal ion uptake and flocculating properties. Based on the above results the synthesized graft copolymers CMGOH-g-NVF, may be exploited as potential candidates for some of the important applications such as superabsorption, flocculation and other similar applications.

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