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Graft (partially carboxymethylated guar gum-g-poly vinyl sulfonic acid) copolymer: From synthesis to applications

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ABSTRACT

The aim of the paper is to study the physico-chemical phenomenon of synthesized graft copolymer (carboxymethylated guar gum-g-vinylsulfonic acid). The reaction optimum conditions for grafting has also been determined by studying the effect of vinylsulfonic acid, hydrogen ion, peroxymonosulphate, glycolic acid concentration and carboxymethylated guar gum along with time and temperature. Experimental results show that maximum grafting has been obtained at 1.8 g dm^{-3} concentration of partially carboxymethylated guar gum and 5.3×10^{-2} mol dm^{-3} concentration of vinylsulfonic acid. It has been observed that grafting ratio, add on, conversion, efficiency increase up to 4.0×10^{-3} mol dm^{-3} of hydrogen ion, 4×10^{-3} mol dm^{-3} of glycolic acid, 14×10^{-3} mol dm^{-3} of peroxymonosulphate and 35 °C of temperature. Grafted copolymer has been characterized by FTIR spectroscopy and thermogravimetric analysis. Water swelling, flocculating, metal ion uptake and resistance to biodegradability properties of partially carboxymethylated guar gum-g-vinylsulfonic acid have been determined.

1. 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 (Kumar, Srivastava, & Behari, 2009; Mishra, Tripathy, Yadav, Sand, & Behari, 2010; Tripathy, Mishra, Yadav, Sand, & Behari, 2009). To increase the paramount contributions toward their industrial applications, this study has been performed, which is concerned with the synthesis of a new type of graft copolymer (partially carboxymethylated guar gum-g-Vinyl sulfonic acid). Partially carboxymethylated guar gum [CmgOH; degree of substitution (DS) = 0.291] has been chosen as backbone (Thaker & Trivedi, 2005) which is derivative of naturally occurring guar gum and constituted of galactomannan polysaccharide isolated from the seed endosperm and having linear chain β-D-mannopyranose joined by (1–4) linking with α-D-galactopyranosyl units (Sinha & Kumria, 2001) attached by 1, 6 links in ratio of 1:2. Because of the immense potential and low price, this versatile polymer is used as a vehicle for oral controlled release purpose (Guo, Skinner, Harcum, & Barnum, 1998). Guar gum and its derivatives find numerous other applications, such as in oil industry. They also act as major ingredients in drilling muds and fingering fluids whereas in textile industry help to improve printing quality (Turk & Schneider, 2000). Even though guar gum and its derivatives enjoy wide range of applications, however, like other polysaccharides they suffer from their drawback like easier susceptibility of microbial attack. The grafting provides an efficient route not only removing the drawback but also improving its properties toward swelling and flocculation. Up to date many investigations have been carried out in view of preparing biopolymer based advanced materials, but reports on grafting onto the partially carboxymethylated guar gum are scantily available in the light of its versatile applications. Poly(vinylsulfonic acid, sodium salt) (PVSA) has negatively chargeable sulfonate groups and is a blood-compatible material. Many researchers (Kim, Park, & Kim, 2004) have reported that the incorporation of sulfonate groups into substrates reduces protein adsorption or platelet adhesion, due to the negatively charged character of these groups, in aqueous solutions. Lee and Oh (2002) reported that negatively chargeable sulfonate groups may be very good for improved blood compatibility. Okayasu, Saito, Nishide, and Hearn Milton (2009)reported that poly(vinylsulfonic acid) (PVSA) has a high acid density (ion-exchange capacity; IEC = 9.2 mequiv. g^{-1}) and is the solid-state analog of sulfuric acid. PVSA is expected to have various applications, such as strong cationic exchange, for water retention, and as an acid catalyst. Therefore, present work aimed to prepare graft copolymer of partially carboxymethylated guar gum and vinyl sulfonic acid so that to develop a product with high water swelling capacity and could be exploited industrially for metal ion sorption

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and flocculation. Synthesis of carboxymethylated guar gum-g-vinyl sulfonic acid has been done using peroxymonosulphate/glycolic acid redox pair under nitrogen atmosphere.

2. Experimental

2.1. Materials

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

2.2. Procedure for graft copolymerization

For each experiment partially carboxymethylated guar gum solution has been prepared by addition of weighed amount of partially carboxymethylated guar gum (0.4–1.8 g dm^{-3}) into reactor containing triple distilled water with rapid stirring in reactor. The calculated amount of vinylsulfonic acid (1.3–6.7 $\times$ 10^{-2} mol dm^{-3}), potassium peroxymonosulphate (0.2–1.8 $\times$ 10^{-2} mol dm^{-3}), glycolic acid (1.6–4.8 $\times$ 10^{-3} mol dm^{-3}), sulphuric acid (0.4–1.2 $\times$ 10^{-2} mol dm^{-3}), solutions has been added to the reactor at constant temperature and a slow stream of pure nitrogen is passed. After 30 min, a known amount of deoxygenated potassium peroxymonosulphate, solution is added to initiate the reaction. The experiments were done in pure nitrogen gas. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring it in to water/methanol mixture (ratio 1:5). The grafted sample has been separated by filtration and then dried and weighed.

2.3. Separation of homopolymer

The filtrate has been concentrated by distillation under reduced pressure in the presence of little of amount hydroquinone. The poly vinyl sulfonic acid was precipitated by pouring concentrated filtrate into pure methanol. The poly vinyl sulfonic acid thus obtained, has been separated, dried and weighed.

2.4. Characterization of graft copolymer

The graft copolymer has been characterized as reported in our previous publication (Yadav, Sand, Mishra, & Behari, 2010)

2.5. Study of properties

2.5.1. Swelling

Swelling studies have been done as reported in our previous publication (Yadav, Mishra, & Behari, 2011).

2.5.2. Metal ion sorption test

The metal ion sorption studies of graft copolymer has been reported in our previous publication (Yadav, Mishra, Sand & behari, 2011).

2.5.3. Flocculation

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

Table 1
Effect of PMS concentration [Cmg] = 1.0 g dm^{-3}, [VSA] = 4 $\times$ 10^{-2} mol dm^{-3}, [H$^+$] = 8 $\times$ 10^{-3} mol dm^{-3}, temp. = 35 °C, time = 120 min, [GA] = 3.2 $\times$ 10^{-3} mol dm^{-3}.

[PMS] $\times$ 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
2	50.6	28.9	33.6	14.5	71.1
6	102.0	44.9	50.5	24.4	55.1
10	134.5	51.6	57.4	30.8	48.4
14	328.0	73.0	76.6	67.1	27.0
18	360.5	75.6	83.4	72.4	24.4

2.5.4. Resistance to biodegradability

Resistance to biodegradability of carboxymethylated guar gum and carboxymethylated guar gum-g-vinylsulfonic 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.

2.6. Method of characterization of graft copolymer (partially carboxymethylated guar gum-g-vinylsulfonic acid)

2.6.1. IR spectroscopy

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

2.6.2. Thermogravimetric analysis

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

3. Results and discussions

3.1. Determination of optimum grafting conditions

The optimum reaction conditions for maximum percentage of grafting of vinylsulfonic acid onto partially carboxymethylated guar gum by using potassium peroxymonosulphate (PMS)/glycolic acid redox system in the presence of hydrogen ion (H$^+$) have determined.

3.1.1. Effect of concentration of peroxymonosulphate

The effect of peroxymonosulphate ion concentration on grafting reaction has been studied and the results were summarized in Table 1. It was observed that grafting ratio, efficiency and add on were increased on increasing the peroxymonosulphate concentration from 2 $\times$ 10^{-3} to 14 $\times$ 10^{-3} mol dm^{-3} and thereafter grafting ratio, efficiency and add on were decreased. The enhancement in grafting parameters within cited range of peroxymonosulphate concentration was due to the progressive reduction of potassium peroxymonosulphate producing greater number of free radicals. These radicals attack on the partially carboxymethylated guar gum molecule creating more radical sites onto which monomers addition takes place. But beyond the cited range, grafting parameters were decreased because of the presence of large number of free radicals, which may terminate the growing grafted chain by oxidative termination.

3.1.2. Effect of concentration of glycolic acid

The variation of concentration of glycolic acid (GA) from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3} reveals that of grafting ratio(%*G* = 85.2–256.6), add on (%*A* = 46–72), conversion (%*C* = 18–55.2) and efficiency (%*E* = 44–66.3) increase on increasing the glycolic acid concentration up to 4.0×10^{-3} mol dm^{-3} due to availability of more primary free radicals ($R^{\bullet} = R_1S^{\bullet}$ and $SO_4^{\bullet -}$), which might be formed due to progressive reduction of PMS by glycolic. However, on further increasing the concentration of glycolic acid from 4.0×10^{-3} to 4.8×10^{-3} mol dm^{-3}, the decrement in grafting parameters (%*G* = 256.6–226, %*A* = 72–69, %*C* = 55.2–47.4, %*E* = 66.3–65.2) has been found which is probably due to the premature termination of vinylsulfonic acid radicals which will cause to give more homopolymer.

3.1.3. Effect of concentration of partially carboxymethylated guar gum

The effect of concentration of partially carboxymethylated guar gum has been observed with an aim to study the effect of its concentration (from 0.4 to 1.8 g dm^{-3}) on grafting parameters. It is obtained that the grafting parameters increase continuously on increasing the concentration of partially carboxymethylated guar gum (Fig. 1a). This may be due to greater availability of grafting site at partially carboxymethylated guar gum.

3.1.4. Effect of concentration of hydrogen ion

To examine the effect of hydrogen ion concentration on grafting parameters, the reaction has been carried out at various concentration of sulfuric acid and results are shown in. The grafting ratio, add on, and efficiency have been found to decrease continuously with increase in concentration of sulfuric acid from 4×10^{-3} to 12×10^{-3} mol dm^{-3} (Fig. 1b). This behavior might have occurred due to the formation of inactive H_2SO_5 species (Mishra, Tripathy, Srivastava, Pandey, & Behari, 2009), thus the concentration of HSO_5^- decreased, resulting in production of less primary free radicals.

3.1.5. Effect of concentration of vinylsulfonic acid

The effect of concentration of vinylsulfonic acid on grafting parameters has been investigated by varying the concentration of vinylsulfonic acid (VSA) from 1.3×10^{-2} to 6.7×10^{-2} mol dm^{-3}. It has been observed that grafting ratio, add on and efficiency increase on increasing the concentration up to 5.3×10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease (Fig. 1c). 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 partially carboxymethylated guar gum macro radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighboring molecules leading to propagation. But on further increasing the concentration of vinylsulfonic acid, the grafting parameters decrease due to formation of more homopolymer.

3.1.6. Effect of temperature

The effect of temperature on grafting parameters has been studied from 25 to 45 °C. It has been observed that grafting ratio, add on, and efficiency increases (%*G* = 110.2–165.1, %*A* = 52.4–62.3, %*E* = 47.6–58.5) continuously on increasing the temperature. The increment in grafting ratio, add on, and efficiency is attributed to the fact that the rate of production of primary free radicals increases and movement of vinylsulfonic acid to partially carboxymethylated guar gum free radicals also increased which increase the value of grafting parameters.

3.1.7. Effect of time

The effect of time period on grafting parameters has been studied by varying the time period of the reaction from 60 to 180 min. It has been observed that grafting ratio, add on, and efficiency increase continuously with increase in time period which leads to increase in the rate of production of radicals, hence increase in grafting parameters has been observed (Fig. 1d).

3.2. Mechanism

On the basis of experimental results, the following tentative mechanism has been proposed for graft copolymerization of vinylsulfonic acid (VSA) onto partially carboxymethylated guar gum using peroxymonosulphate (PMS) and glycolic acid redox pair. Initially peroxymonosulphate (PMS) reacts with glycolic acid to form a complex the complex dissociates to yield radicals according to following scheme.

$$CH_2(OH).COOH + HSO_5^- \longrightarrow \text{Complex}$$

$$\text{Complex} \longrightarrow \begin{cases} \overset{\bullet}{C}H(OH)COOH + SO_4^- + H_2O \quad \text{(A)} \\ CH_2(OH)COO^{\bullet} + SO_4^- + H_2O \quad \text{(B)} \\ \overset{\bullet}{C}H_2(OH) + CO_2 + H_2O + SO_4^{\bullet -} \quad \text{(C)} \end{cases}$$

$$\text{Where } R^{\bullet} = \text{(A), (B), (C) and } SO_4^{\bullet -}$$

The R• radicals abstract hydrogen atom from partially carboxymethylated guar gum molecule producing partially carboxymethylated guar gum radical. The monomer molecules, which are in close vicinity of reaction sites, become acceptor of partially carboxymethylated guar gum radicals, resulting in chain initiation and thereafter themselves become free radical donor to neighboring molecules leading to propagation. These grafted chains are terminated by coupling to give graft copolymer.

3.3. Evidence of grafting

3.3.1. IR spectroscopy

The infra red spectra analysis has been utilized to prove grafting, for these IR spectra of partially carboxymethylated guar gum (Yadav, Sand, Mishra, & Behari, 2010). And partially carboxymethylated guar gum-g-vinylsulfonic acid, have been recorded in the range of 500–4000 cm^{-1}. On comparing the IR spectra of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-vinylsulfonic acid (Fig. 2), a band at 3450.0 cm^{-1} is due to OH stretching vibration in the spectrum of partially carboxymethylated guar gum shifting to 3444.1 cm^{-1} in partially carboxymethylated guar gum-g-vinylsulfonic acid, indicates the participation of hydroxyl groups in grafting process. The grafting is further confirmed by characteristic absorption band of —SO_2—O— stretching vibration at 1184.1 cm^{-1} of monomer molecule in partially carboxymethylated guar gum-g-vinylsulfonic acid. The appearance of additional peaks in spectrum of graft copolymer and shifting of OH stretching vibration appeared in the spectrum of partially carboxymethylated guar gum-g-vinylsulfonic acid from partially carboxymethylated guar gum showed that grafting might have taken place on OH sites of partially carboxymethylated guar gum molecules.

3.3.2. Thermogravimetric analysis

Thermogravimetric curve of partially carboxymethylated guar gum (Yadav, Sand, Mishra, & Behari, 2010) shows single step degradation. The weight loss 1.5% is due to loss absorbed water

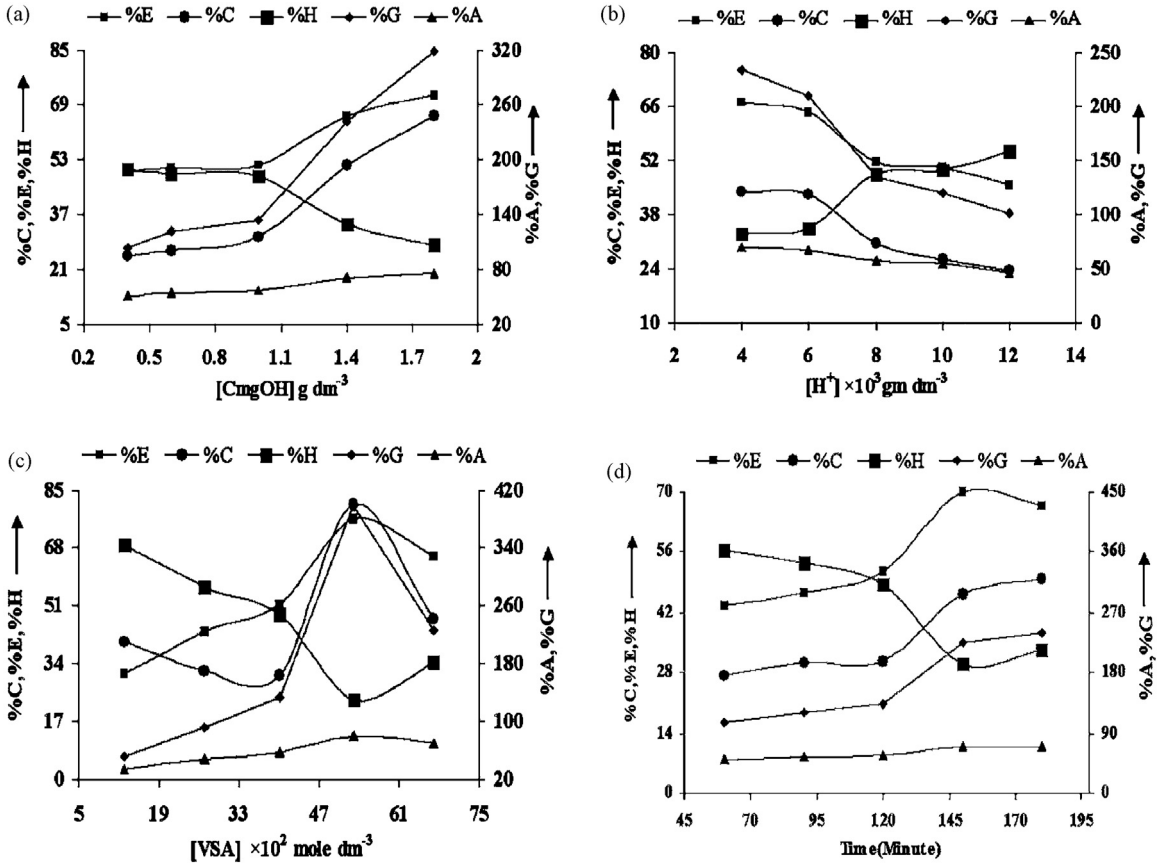

Fig. 1. (a) Effect of partially carboxymethylated guar gum concentration. (b) Effect of sulfuric acid concentration. (c) Effect of vinylsulfonic acid concentration. (d) Effect of time.

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

$$\text{IPDT}(^\circ\text{C}) = A * K * (T_f - T_i) + T_i \quad (1)$$

$$A* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \quad (2)$$

$$K* = \frac{S_1 + S_2}{S_1} \quad (3)$$

where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, T_i the initial experimental temperature, T_f the final experimental temperature. Fig. 4 shows a representation of S_1, S_2 and S_3 for calculating A^* and K^*. The integral procedural decomposition temperature (IPDT) is 189 °C. T_{max}, the temperature at which maximum degradation occurred, is 268 °C and final decomposition temperature (FDT) has been observed at approximately 900 °C. But in case of partially carboxymethylated guar gum-g-vinylsulfonic, the weight loss 1.4% at approximately 50 °C might be due to loss of absorbed water. The polymer decomposition temperature (PDT) was found at approximately75 °C. Partially carboxymethylated guar gum-g-vinylsulfonic acid shows three step degradations (Fig. 3). It has been found that degradation of partially carboxymethylated carboxymethylated guar gum-g-vinylsulfonic starts at approximately 100 °C temperature. The rate of weight loss increases with increase in temperature from 105 °C to 148 °C and there after decreases and attains maximum at approximately 737 °C. First T_{max}, 233 °C is due to elimination of CO_2 molecule which also confirmed by a peak appeared in DTA (Differential Thermal Analysis) curve of partially carboxymethylated guar gum. The second T_{max}, is 345 °C is due to elimination of SO_2 molecule, confirmed by a peak appeared at approximately 350 °C in DTA curve

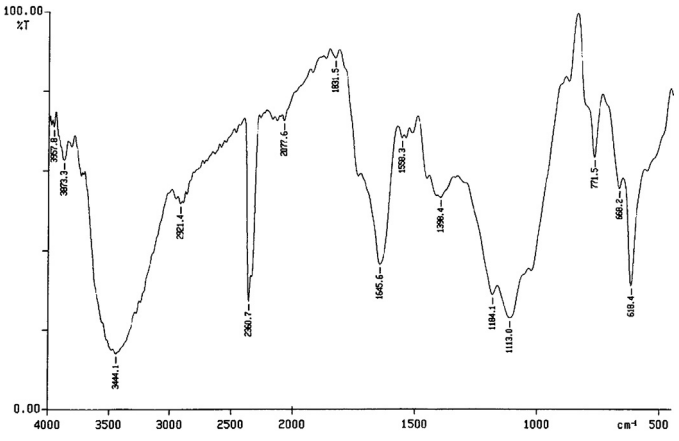

Fig. 2. IR spectrum of partially carboxymethylated guar gum-g-vinylsulfonic acid.

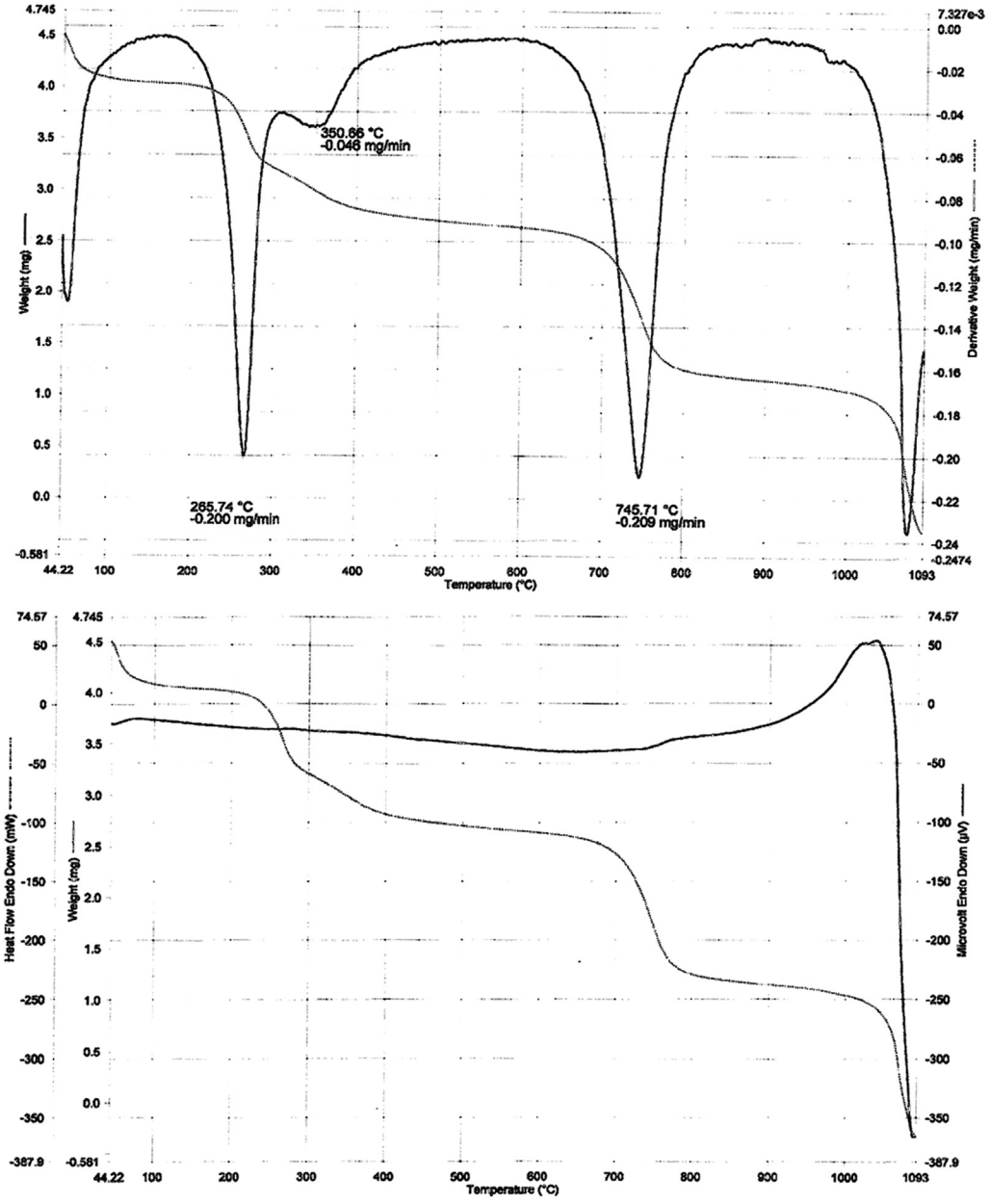

Fig. 3. Thermogravimetric trace of partially carboxymethylated guar gum-g-vinylsulfonic acid.

and the third T_{max} at 737 °C is due to elimination of —OH group from pendent chains attached to partially carboxymethylated guar gum. The integral procedural decomposition (IPDT) and final decomposition temperature (FDT) have been found at approximately 305 °C and 900 °C respectively. On comparing the thermograms of parent backbone (partially carboxymethylated guar gum) and graft copolymer (partially carboxymethylated guar gum-g-vinylsulfonic acid), it has been observed that final and integral procedural decomposition temperature have been found to be higher for graft copolymer. This indicates that graft copolymer is thermally stable than backbone.

3.4. Study of the properties

3.4.1. Swelling test

The results of swelling studies reveal that swelling of graft copolymer is dependent upon percent grafting. Since the increment in percent grafting is directly related with monomer concentration, thus water retention capacity and hydrophilicity is increased with increase in concentration of vinylsulfonic acid. It has been observed that a maximum percent swelling of 110.4% is obtained when grafting ratio is 434. With the increase in grafting ratio (%*G* increases from 400.5–434.5), the length of pendent of poly (vinylsulfonic acid) increases which helps in holding more water, thereby increases the swelling capacity of graft copolymer.

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

The results of sorption behavior of partially carboxymethylated guar gum and its grafted polymer with vinylsulfonic acid have been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r). The results are given in Table 2. It has been observed that the values of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly as percent grafting increases, which might be due to the fact that as grafting increases, the sorption sites for metal ions are increased

Table 2
Metal ion sorption [Cmg] = 1.0 g dm^{-3}, [PMS] = 10 × 10^{-3} mol dm^{-3}, [H$^+$] = 8 × 10^{-3} mol dm^{-3}, time = 120 min., [GA] = 3.2 × 10^{-3} mol dm^{-3}, temp. = 35 °C.

Sample[a]		CmgOH	A	B	C	D	E
[VSA] × 10^2 mol dm^{-3}		–	1.3	2.7	4.0	5.3	6.7
% grafting		–	52.3	92.0	134.5	398.0	226.0
Percent uptake (P_u)	Pb^{2+}	1.0	1.8	4.0	5.5	9.1	7.5
	Ni^{2+}	2.5	3.5	6.5	8.7	12.0	11.0
	Zn^{2+}	2.2	2.8	5.3	7.2	10.0	9.1
Partition coefficient (K_d)	Pb^{2+}	7.5	9.0	19.5	27.2	48.5	46.0
	Ni^{2+}	13.7	17.5	33.5	45.2	59.5	58.0
	Zn^{2+}	10.9	14.0	26.0	35.0	53.0	50.0
Retention capacity (Q_r)	Pb^{2+}	1.0	1.5	2.1	2.6	4.1	3.8
	Ni^{2+}	1.2	2.1	3.5	4.6	5.8	6.1
	Zn^{2+}	1.5	1.8	2.8	3.8	5.0	4.5

[a] A, B, C, D and E are graft copolymer samples prepared.

due to availability of additional functional groups of monomer grafted i.e. vinylsulfonic acid and increment in sorption capacity takes place due to the incorporation of its pendant chain of poly (vinylsulfonic acid), so greater the grafting, greater will be the sorption of metal ion. Results also show that Pb^{2+} was least uptakable in comparison to Zn^{2+} and Ni^{2+} metal ions.

3.4.3. Flocculation properties

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone partially carboxymethylated guar gum and graft copolymer of vinylsulfonic acid with partially carboxymethylated guar gum. Plots of supernatant turbidity versus polymer dosage for coking and noncoking coals are presented in Fig. 5. It is evident that grafted copolymer (partially carboxymethylated guar gum-g-vinylsulfonic acid) shows better performance with low turbidity than partially carboxymethylated guar gum itself. In grafted copolymer, the dangling of poly (vinylsulfonic acid) chains has better approachability (Deshmukh, Singh, & Chaturvedi, 1985) to the contaminant coal particles hence increasing its flocculation capability. Here the bridging mechanism operates (Gregory, 1982), which involves binding or bridging individual particles to form flocs, hence increases its flocculation.

3.4.4. Resistance to biodegradability of partially carboxymethylated guar gum and its graft copolymer

The results presented in the form of graph in (Fig. 6). From efflux time of polymer solution (t) and that of solvent 1.0 M $NaNO_3$ (t_0), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of partially carboxymethylated guar gum-g-vinylsulfonic acid is lower than partially carboxymethylated guar gum (Fig. 6). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Ungeheur, Bewersdorff, & Singh, 1989). Partially carboxymethylated guar gum solution, like other polysaccharide

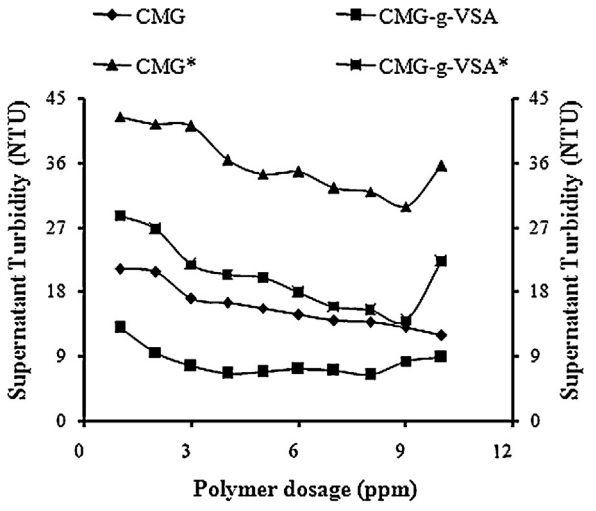

Fig. 5. Effect of polymer dosage on turbidity for coking coal and non coking coal*.

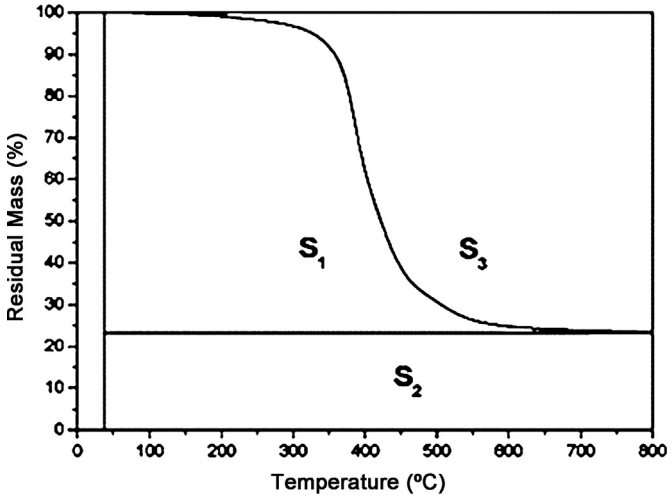

Fig. 4. Schematic representation of S_1, S_2, and S_3 for A^* and K^*.

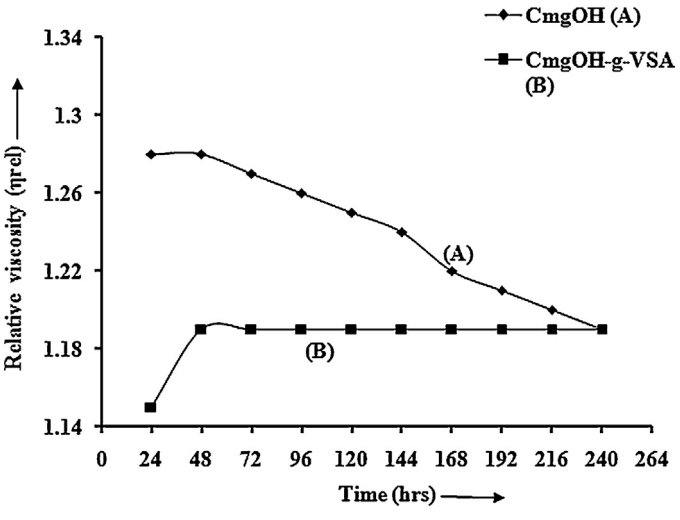

Fig. 6. Resistance to biodegradability of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-vinylsulfonic acid.

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. 6, 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. 6, Line B). These results show that the graft copolymer is less susceptible to biodegradation and similar results have also been reported by others (Deshmukh et al., 1985). This is in an agreement with the fact that by incorporating relatively poly (vinylsulfonic 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 (vinylsulfonic acid) graft onto partially carboxymethylated guar gum through graft copolymerization, the drag reduction effectiveness can be enhanced and biodegradation can be minimized.

4. Conclusion

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

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.02.084.

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