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Synthesis of graft copolymer (CmgOH-g-NVP) and study of physicochemical properties: Characterization and application

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ABSTRACT

The synthesis of graft copolymer (partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone) is carried out in nitrogen atmosphere using potassium peroxymonosulphate and glycolic acid as redox system. The effect of reaction variables including the concentration of N-vinyl-2-pyrrolidone (8×10^{-2} to 24×10^{-2}) mol dm^{-3}, potassium peroxymonosulphate (6×10^{-3} to 22×10^{-3}) mol dm^{-3}, glycolic acid (0.6×10^{-3} to 4.0×10^{-3}) mol dm^{-3}, sulphuric acid (1×10^{-3} to 3×10^{-3}) mol dm^{-3}), partially carboxymethylated guar gum (0.6–1.4) g dm^{-3} as well as time duration (60–180) min and temperature (30–50) °C has been studied. The water swelling capacity of graft copolymer is investigated. Flocculation property for both coking and non-coking coals is studied for the treatment of coal mine waste water. The graft copolymer has been characterized by Fourier transform infrared spectroscopy and thermogravimetic analysis.

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 (Mishra, Yadav, Tripathy, Sand, & Behari, 2010; Sand, Yadav, & Behari, 2010; Sand, Yadav, Mishra, & Behari, 2010). 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-vinyl-2-pyrrolidone). 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 (Skinner, Harcum, Barnum, & Guo). 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 & Reinhold, 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 (Srivastava, Tripathy, Mishra, & Behari, 2007). 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 CmgOH are scantily available in the light of its versatile applications. This work is carried out with an aim to tailor partially carboxymethylated guar gum based hybrid material by grafting of N-vinyl-2-pyrrolidone. In the present article, grafting of N-vinyl-2-pyrrolidone onto the backbone of partially carboxymethylated guar gum has been reported with the objective of increasing the applications of partially carboxymethylated guar gum. N-vinyl-2-pyrrolidone, which is hydrophilic and non-toxic monomer, has various industrial applications (Duan, 1993; Gaenger & Florig, 2007; Suzuki, Fukuda, & Yoneto, 1993). It has been used as a main component of temporary skin covers or wound dressing (Nho & Park, 2002) and also wrapping material (Ausman et al., 2001) of single-walled carbon nanotubes (SWNTs). Prompted by the applications of partially carboxymethylated guar gum and N-vinyl-2-pyrrolidone, the hitherto unreported graft copolymer viz. partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone was prepared by employing potassium peroxymonosulphate/glycolic acid redox system. For optimization of grafting conditions, the effect of potassium peroxymonosulphate, glycolic acid, hydrogen ion, partially

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carboxymethylated guar gum and N-vinyl-2-pyrrolidone concentration along with the time and temperature has been investigated.

2. Experimental

2.1. Materials

N-vinyl-2-pyrrolidone (Sigma–Aldrich, Gillingham, Dorset, UK) was freshly distilled at 11 mm Hg and 60 °C and only middle fraction was used. Potassium peroxymonosulphate purchased from Du Pont (USA) and glycolic acid (E. Merck, India) are of analytical grades and used as such without further purification. Partially carboxymethylated guar gum was received as a gift sample from Hindustan Gums and Chemicals, India. For maintaining hydrogen ion concentration, sulphuric acid (E. Merck, India) 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 used were received from Steel Plant, Bokaro, India.

2.2. Procedure for grafting

All the reactions have been carried out in nitrogen atmosphere. For each experiment, partially carboxymethylated guar gum solution was prepared by slow addition of calculated amount of partially carboxymethylated guar gum into three necked flask reactor containing distilled water. A calculated amount of N-vinyl-2-pyrrolidone, glycolic acid and sulphuric acid solutions were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium peroxymonosulphate solution was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen free nitrogen gas at constant temperature. After desired time period, the reaction was stopped by letting air into reactor. The grafted sample was precipitated by pouring it into the water/methanol mixture ratio (1:4). The precipitate was separated, dried and weighed. The poly (N-vinyl-2-pyrrolidone) is remained in the filtrate. To the filtrate a pinch of hydroquinone was added and concentrated by distillation under reduce pressure. The poly (N-vinyl-2-pyrrolidone) was precipitated by pouring into the pure methanol. The poly (N-vinyl-2-pyrrolidone) thus obtained was separated, dried and weighed.

2.3. Study of properties

2.3.1. Swelling test

Swelling studies have been carried out with different grafted samples synthesized by varying the concentration of N-vinyl-2-pyrrolidone. The desired amount of each grafted sample (0.02 g) has been taken and immersed in 20 ml of 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. The percent swelling (P_s) and swelling ratio (S_r) are calculated by using expression (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000):

$$\text{Percent swelling}\,(P_s) = \text{Swelling ratio}\,(S_r) \times 100$$

$$\text{Swelling ratio}\,(S_r) = \frac{\text{Weight of swollen sample} - \text{weight of dry sample}}{\text{Weight of dry sample}}$$

2.3.2. Metal ion sorption test

The metal ion sorption study has been carried out by using different samples of graft copolymers, which have been synthesized by varying the concentration of N-vinyl-2-pyrrolidone from (8.0×10^{-2} to 24.0×10^{-2}) mol dm^{-3}. For carrying 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 behaviour of partially carboxymethylated guar gum and its graft polymer synthesized (partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone) have been investigated in terms of different parameters i.e. percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r) (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998):

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

$$\text{Partition coefficient}\,(K_d) = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution (ml)}}{\text{Weight of dry polymer}}$$

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

2.3.3. Flocculation test

In 1.0 l beaker, 200 ml of 1.0 wt.% coal suspension was taken. The stirrer blade of the flocculator was dipped in the suspension. Under a low stirring condition, required quantity of polymer solution was added to a 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.).

2.3.4. Resistance to biodegradability

Resistance to biodegradability of partially carboxymethylated guar gum and graft copolymer (partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone) has been measured in terms of viscosity and the viscosity is calculated with the help of Ubbelohde capillary viscometer at constant temperature i.e. at 30 °C.

2.4. Characterization

2.4.1. FTIR analysis

The infrared spectra analysis has been carried to prove grafting. For this, the IR spectra of ungrafted and grafted samples in KBr pellets have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1}.

2.4.2. TGA analysis

The thermal analysis of partially carboxymethylated guar gum and graft copolymer (partially carboxymethylated guar gum-N-vinyl-2-pyrrolidone) has been carried in inert atmosphere at heating rate of 15 °C/min within temperature range from 0 °C to 1400 °C on NETZSCH-STA 409C/CD thermal analyzer.

3. Results and discussion

3.1. Grafting properties

The graft copolymer has been characterized as reported in the literature (Fanta, 1973a, 1973b):

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

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

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

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

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

3.2. Determination of optimum reaction conditions

The effect of potassium peroxymonosulphate (PMS), glycolic acid (GA), sulphuric acid (H^+), N-vinyl-2-pyrrolidone (NVP), partially carboxymethylated guar gum concentrations, reaction time and temperature on grafting parameters has been studied.

3.2.1. Effect of potassium peroxymonosulphate concentration

The effect of potassium peroxymonopersulphate on grafting parameters has been studied by varying the concentration of potassium peroxymonopersulphate from (0.6×10^{-2} to 2.2×10^{-2}) mol dm^{-3}. It has been found that the grafting ratio, add on and conversion increase i.e. (%G increases from 159.6 to 667.7, %A increases from 61.4 to 86.4, %C increases from 22.6 to 62.4) on increasing the concentration of potassium peroxymonopersulphate from (0.6×10^{-2} to 2.2×10^{-2}) mol dm^{-3}. This behaviour might be attributed to the progressive reduction of potassium peroxymonopersulphate by glycolic acid producing primary free radicals, which attack on the partially carboxymethylated guar gum molecules creating more active sites, to which addition of N-vinyl-2-pyrrolidone molecules take place.

3.2.2. Effect of glycolic acid concentration

The effect of glycolic acid concentration on graft copolymerization has been studied by varying its concentration from (0.8×10^{-3} to 4×10^{-3}) mol dm^{-3}. It has been observed that the grafting ratio, efficiency and add on increase i.e. (%G increases from 405.2 to 482.7, %E increases from 57.1 to 84.2, %A increases from 80.2 to 82.9) on increasing glycolic acid concentration up to 2.4×10^{-3} mol dm^{-3} and thereafter grafting ratio, efficiency and add on decrease i.e. (%G decreases from 482.7 to 397, %E decreases from 84.2 to 60.4, %A decreases from 82.9 to 79.8). The former effect could be explained due to increase in number of primary free radicals formed [$^\bullet CH(OH)COOH$, $CH_2(OH)COO^\bullet$, $^\bullet CH_2(OH)$ and $SO_4^{\cdot-}$], however at high concentration of glycolic acid i.e. beyond 2.4×10^{-3} mol dm^{-3}, the formation of poly (N-vinyl-2-pyrrolidone) increases, which in turn decreases grafting efficiency.

3.2.3. Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the reaction has been carried out at various concentrations of sulphuric acid i.e. from (1.0×10^{-3} to 3.0×10^{-3}) mol dm^{-3} and results have been presented in Table 1. It has been found that the grafting ratio, add on, and efficiency increase on increasing the concentration of hydrogen ion up to 2.0×10^{-3} mol dm^{-3}. However, beyond this concentration grafting ratio, add on, and efficiency decrease while conversion and homopolymer increase. This behaviour might be due to the formation of H_2SO_5 as an inactive species (Pandey, Banerjee, Taunk, & Behari, 2003), thus the concentration of HSO_5^- decreases resulting in less production of primary free radicals, thereby decreasing the grafting parameters:

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

Table 1
Effect of hydrogen ion concentration.

[H^+] ($\times 10^3$ mol dm^{-3})	%G	%E	%A	%C	%H
1.0	437.0	55.3	81.3	44.4	44.6
1.5	466.5	59.7	82.3	43.9	40.2
2.0	482.7	84.2	84.9	32.2	28.3
2.5	453.3	70.4	81.9	36.1	29.5
3.0	440.0	65.4	81.4	37.8	34.5

[CmgOH] = 1.0 g dm^{-3}, [PMS] = 1.4×10^{-2} mol dm^{-3}, [GA] = 2.4×10^{-3} mol dm^{-3}, [H^+] = 2×10^{-3} mol dm^{-3}, temperature = 40 °C, and time = 120 min.

3.2.4. Effect of partially carboxymethylated guar gum concentration

The effect of concentration of partially carboxymethylated guar gum on grafting parameters has been studied by varying the concentration of partially carboxymethylated guar gum from 0.6 to 1.4 g dm^{-3}. As the concentration of partially carboxymethylated guar gum is increased from 0.6 to 1.0 g dm^{-3}, grafting ratio, efficiency and add on increase i.e. (%G increases from 403.7 to 482.7, %E increases from 62.3 to 84.2, %A increases from 80.1 to 82.9). This is due to greater availability of grafting sites at partially carboxymethylated guar gum molecules. The concentration is further increased beyond 1.0 g dm^{-3}, the viscosity of reaction mixture increases, which hinders the movement of free radicals, thereby, decreasing the grafting parameters (%G decreases from 482.7 to 467.7, %E decreases from 84.2 to 75.3, %A decreases from 82.9 to 82.3).

3.2.5. Effect of N-vinyl-2-pyrrolidone concentration

The effect of N-vinyl-2-pyrrolidone (NVP) concentration on graft copolymerization has been studied by varying its concentration in from (8×10^{-2} to 24×10^{-2}) mol dm^{-3}. It has been observed that grafting ratio, add on and efficiency increase i.e. (%G increases from 400.5 to 482.7, %E increases from 66.3 to 84.2, %A increases from 80.0 to 82.9) on increasing the concentration of N-vinyl-2-pyrrolidone from (8×10^{-2} to 16×10^{-2}) mol dm^{-3}. This increment can be explained due to greater availability of monomer molecules at the close proximity to the polymeric backbone. The monomer molecules, which are at immediate vicinity of reaction sites become acceptors of partially carboxymethylated guar gum macro-radicals ($CmgO^\bullet$) resulting in chain initiation and thereafter themselves become free radical donors to neighbouring molecules leading to lowering of termination. But beyond 16×10^{-2} mol dm^{-3}, grafting parameters decrease (%G decreases from 482.7 to 434.5, %E decreases from 84.2 to 65.6, %A decreases from 82.9 to 81.2) might be due to the formation of more homopolymer, which increases the viscosity of reaction medium due to which movement of free radicals is hindered.

3.2.6. Effect of time

The effect of change in duration of grafting reaction has been studied by varying the time interval from 60 to 180 min. It has been observed that grafting ratio, efficiency and add on increase i.e. (%G increases from 404.5 to 482.7, %E increases from 76.8 to 84.2, %A increases from 80.1 to 82.9) on increasing the time duration from 60 to 120 min. On further increasing the time, grafting parameters show decreasing trend i.e. (%G decreases from 482.7 to 443.1, %E decreases from 84.2 to 63.1, %A decreases from 82.9 to 81.5). This behaviour is explained due to the fact that the propagation of grafting chains takes place due to availability of more active species, which accounts for higher grafting. On further increase in time, the mutual annihilation of growing grafted chains occurs which results in decrement of grafting parameters.

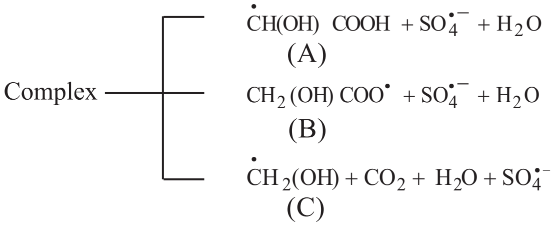
3.2.7. *Effect of temperature*

The effect of temperature on grafting parameters has been studied from 30 °C to 50 °C. It has been observed that as the temperature is increased from 30 °C to 40 °C, there is an increase in values of grafting ratio, efficiency and add on increase i.e. (%G increases from 389.4 to 482.7, %E increases from 51.9 to 84.2, %A increases from 79.5 to 82.9). The increment in these grafting parameters up to 40 °C is due to the increment in production of primary free radicals, resulting in propagation of growing grafted chains. However, beyond 40 °C at higher temperature range, there is decrement in grafting parameters i.e. (%G decreases from 482.7 to 419.7, %E decreases from 84.2 to 57.2, %A decreases from 82.9 to 80.7) which is supported by the fact that potassium peroxymonosulphate decomposes 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 and resulting in the decrement in the grafting parameters.

3.3. *Mechanism*

On the basis of experimental results, the following tentative mechanism has been proposed for graft copolymerization of N-vinyl-2-pyrrolidone onto partially carboxymethylated guar gum using potassium peroxymonosulphate and glycolic acid redox pair. Initially potassium peroxymonosulphate reacts with glycolic acid to form a complex the complex dissociates to yield radicals according to following scheme:

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



$$\text{Complex} \rightarrow \begin{cases} \dot{C}H(OH)\ COOH + SO_4^{\bullet -} + H_2O & \text{(A)} \\ CH_2(OH)\,COO^{\bullet} + SO_4^{\bullet -} + H_2O & \text{(B)} \\ \dot{C}H_2(OH) + CO_2 + H_2O + SO_4^{\bullet -} & \text{(C)} \end{cases}$$

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

The $R^{\bullet}$ radicals abstract hydrogen atom from partially carboxymethylated guar gum molecules producing partially carboxymethylated guar gum macro radical. The monomer molecules, which are in close vicinity of reaction sites, become acceptor of partially carboxymethylated guar gum macro-radicals, resulting in chain initiation and thereafter themselves become free radical donors to neighbouring molecules leading to propagation. These grafted chains are terminated by coupling to give graft copolymer.

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:

$$CmgO^{\bullet} + M \rightarrow CmgOM^{\bullet}$$

$$CmgOM^{\bullet} + M \rightarrow CmgOM_1^{\bullet}$$

$$\vdots$$

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

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

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

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

$$\vdots$$

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

Termination:

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

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

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

3.4. *Evidence of grafting*

3.4.1. *IR spectroscopy*

The infra red spectra of guar gum (Kautharapu et al., 2009), poly(N-vinyl-2-pyrrolidone) (Şahiner, Pekel, & Güven, 1999) has been utilized to replicate and to prove the grafting, for this IR spectra of partially carboxymethylated guar gum (Tripathy, Mishra, Srivastava, Mishra, & Behari, 2008; Yadav, Sand, Mishra, & Behari, 2010) and partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone (represented in Fig. 1) have been recorded in the range of 500–4000 cm^{-1}. On comparing the IR spectra of partially carboxymethylated guar gum and partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone, 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 a variation in intensity of OH stretching vibration and shifting of this peak from 3450.0 cm^{-1} to sharp 3447.6 cm^{-1} appeared in partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone respectively, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band at 1653.5 cm^{-1} due to >C=O stretching vibration, and at 1511.1 cm^{-1} due to –CN stretching vibration of N-vinyl-2-pyrrolidone as monomer respectively. The appearance of additional peaks in the spectrum of graft copolymer and shifting of OH stretching vibration from partially carboxymethylated guar gum showed that grafting might have taken place on OH sites of partially carboxymethylated guar gum.

3.4.2. *Thermogravimetric analysis*

Thermogravimetric analysis curve of partially carboxymethylated guar gum (Tripathy et al., 2008; Yadav et al., 2010) shows the degradation which occurs in a single step. The polymer decomposition temperature (PDT) has been found at 210 °C. The 50% weight loss has been found at 275.3 °C due to loss of absorbed water. The rate of weight loss increased with increasing the temperature up to 405 °C but thereafter it decreases. The integral procedural decomposition temperature (IPDT) and temperature at which maximum degradation occurs (T_{max}) have been found at 219 °C and 277.6 °C respectively. The final decomposition temperature (FDT) is 1074.0 °C. The degradation of graft copolymer (partially

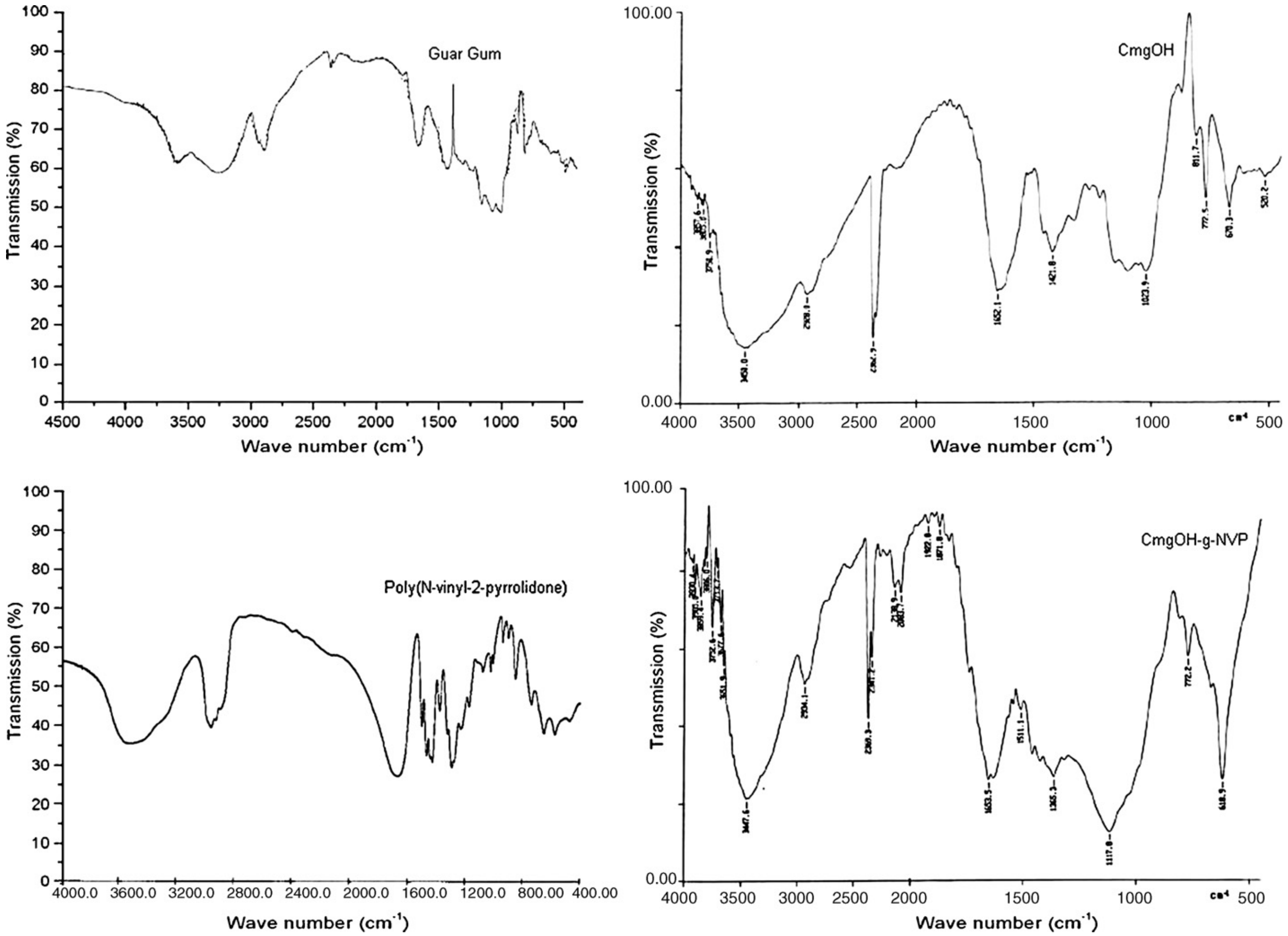


Fig. 1. IR spectrum of guar gum, poly(N-vinyl-2-pyrrolidone), CmgOH and CmgOH-g-N-vinyl-2-pyrrolidone.

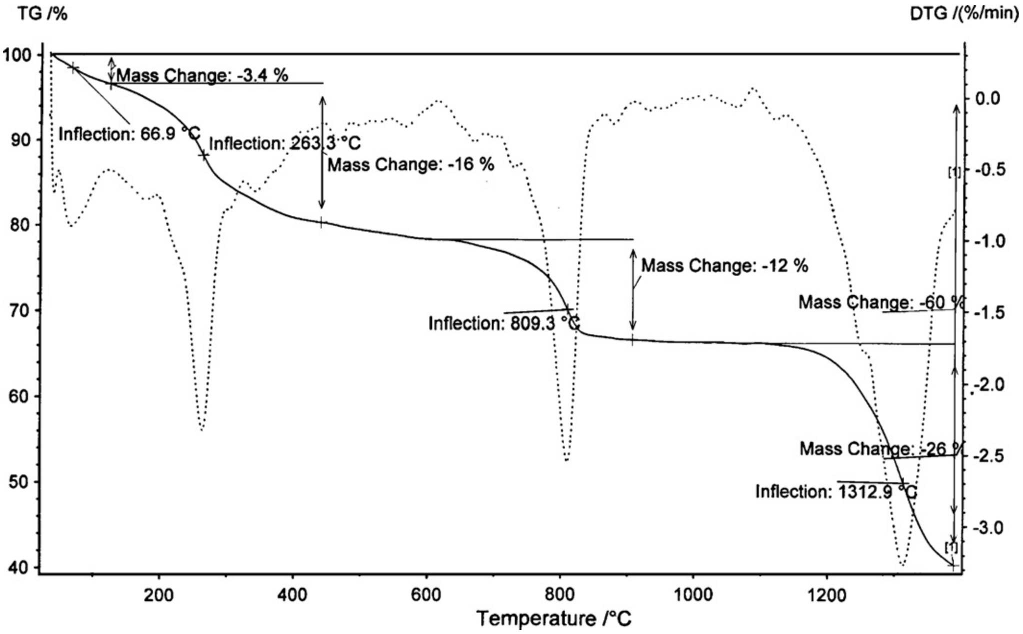


Fig. 2. Thermogravimetric trace of partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone.

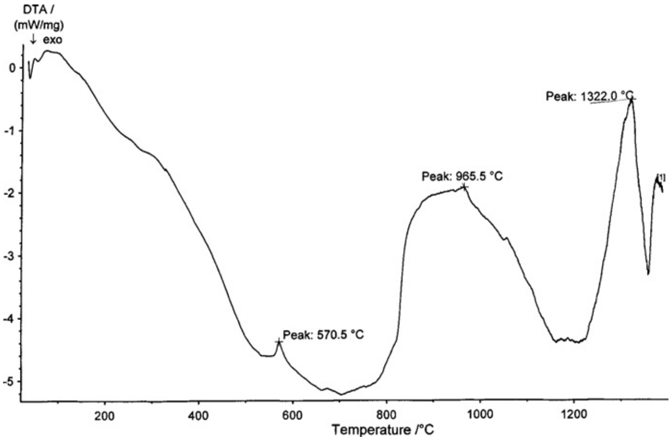


Fig. 3. Differential thermal trace of partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone.

carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone) occurs in three steps (degradation steps are presented in Fig. 2). The weight loss of 3.5% up to 100 °C occurred due to loss of absorbed water. Polymer decomposition temperature (PDT) is found to be near at 225 °C. The differential thermal analysis of graft copolymer (Fig. 3) also shows the gradual degradation with endothermic peak indicating maximum weight loss at 290.9 °C. Only 50% weight loss has been observed at 1306.2 °C. Since the process involves three degradation steps therefore three maximum temperatures (T_{max}) appeared at 263.3 °C, 809.3 °C and 1312.9 °C. First T_{max} at 263.3 °C might be due to elimination of $-CO_2$ from the polymeric backbone, which is also confirmed exothermic peak present in DTA curve of graft copolymer at 570.5 °C. Second T_{max} at 809.3 °C might be due to elimination of five membered ring from pendent chain attached to the polymeric back bone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 965.5 °C. Third T_{max} at 1312.9 °C might be due to elimination of $-H_2$ from pendent chain attached to the polymeric back bone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 1322.0 °C. The integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) and have been found to be at 436.6 °C and 1312.9 °C. The high value of final decomposition temperature (FDT), integral procedural decomposition temperature (IPDT) and three steps degradation indicate that graft copolymer is thermally more stable than partially carboxymethylated guar gum.

3.5. Study of the properties

3.5.1. 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 N-vinyl-2-pyrrolidone. It has been observed that a maximum percent swelling of 110.4% is obtained when grafting ratio is 434.5 (Table 2). With the increase in grafting ratio (%G increases from 400.5 to 434.5), the length of pendent of poly (N-vinyl-2-pyrrolidone) increases which helps in holding more water, thereby increases the swelling capacity of graft copolymer.

3.5.2. Metal ion sorption test

The result of sorption behaviour of partially carboxymethylated guar gum and its grafted polymer with N-vinyl-2-pyrrolidone has been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r). The results are summarized in (Table 3), which depicts 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, pendent chain of poly (N-vinyl-2-pyrrolidone) increases, which offers additional sites for metal ion sorption (Srivastava, Mishra, & Behari, 2010). Thus with the incorporation of more functional groups of poly N-vinyl-2-pyrrolidone, number of sorption sites increase, thereby enhancing the sorption capacity of grafted partially carboxymethylated guar gum as compared to the ungrafted partially carboxymethylated guar gum. The order of selectivity of sorption of metal ions is $Ni^{2+} > Zn^{2+} > Pb^{2+}$.

Table 2
Swelling test.

Sample code[a]	[NVP] ($\times 10^2$ mol dm^{-3})	%G	[Wt. of swollen sample] ($\times 10^2$ g)	P_s	S_r
A	8	400.5	4.04	102.9	1.02
B	12	403.5	4.08	104.4	1.04
C	16	482.7	5.52	176.8	1.76
D	20	438.5	4.22	111.0	1.11
E	24	434.5	4.20	110.4	1.10

[CmgOH] = 1.0 g dm^{-3}, [PMS] = 1.4 × 10^{-2} mol dm^{-3}, [GA] = 2.4 × 10^{-3} mol dm^{-3}, [H$^+$] = 2 × 10^{-3} mol dm^{-3}, temperature = 40 °C, and time = 120 min.

[a] Sample code (A–E) indicates the graft copoymers prepared at different concentrations of N-vinyl-2-pyrrolidone.

Table 3
Metal ion sorption.

Sample code[a]	[NVP] ($\times 10^2$ 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+}
CmgOH[b]	–	–	2.0	1.0	0.9	5.3	2.6	2.3	0.5	0.2	0.2
A	8	400.5	4.1	3.1	2.8	10.8	8.2	7.2	1.0	0.7	0.7
B	12	403.5	6.2	5.3	3.7	16.6	14.0	9.8	1.5	1.2	1.0
C	16	482.7	12.5	10.6	8.4	35.7	29.7	23.1	3.0	2.5	2.2
D	20	438.5	9.3	8.5	7.5	25.8	23.2	20.4	2.5	2.0	2.0
E	24	434.5	7.2	7.4	5.6	19.6	20.1	15.0	1.7	1.7	1.5

[CmgOH] = 1.0 g dm^{-3}, [PMS] = 1.4 × 10^{-2} mol dm^{-3}, [GA] = 2.4 × 10^{-3} mol dm^{-3}, [H$^+$] = 2 × 10^{-3} mol dm^{-3}, temperature = 40 °C, and time = 120 min.

[a] Sample code (A–E) indicates the graft copoymers prepared at different concentrations of N-vinyl-2-pyrrolidone.

[b] Partially carboxymethylated guar gum.

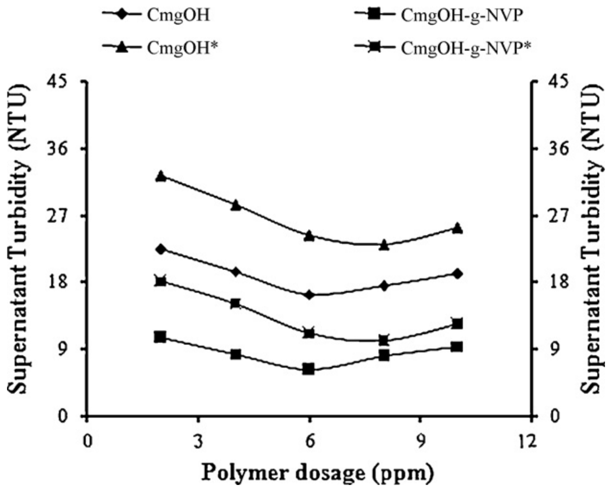


Fig. 4. Effect of polymer dosage on turbidity for coking coal and non coking coal*.

3.5.3. Flocculation test

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 partially carboxymethylated guar gum and graft copolymer of N-vinyl-2-pyrrolidone with partially carboxymethylated guar gum. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in the form of Fig. 4. It has been found that graft copolymer (partially carboxymethylated guar Gum-g-N-vinyl-2-pyrrolidone) 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 (N-vinyl-2-pyrrolidone) chains have better approachability to the contaminant coal particles (Deshmukh, Singh, & Chaturvedi, 1985). Here the bridging mechanism operates (Bratby, 1980), which involves binding or bridging the individual particles to form flocs, hence increases its flocculation capability (Gregory, 1982). By grafting of poly N-vinyl-2-pyrrolidone onto partially carboxymethylated guar gum, efficient flocculants have been obtained.

3.5.4. Resistance to biodegradability

The results presented in the form of graph in Fig. 4. 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-N-vinyl-2-pyrrolidone 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 (Ungeheur, Bewersdorff, & Singh, 1989). Partially carboxymethylated guar gum solution, 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, curve 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, curve B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others (Deshmukh & Singh, 1987). This is in an agreement with the fact that by incorporating relatively poly (N-vinyl-2-pyrrolidone) 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 (N-vinyl-2-pyrrolidone) graft onto partially carboxymethylated guar gum through graft copolymerization, the drag reduction effectiveness can be enhanced and biodegradation can be minimized.

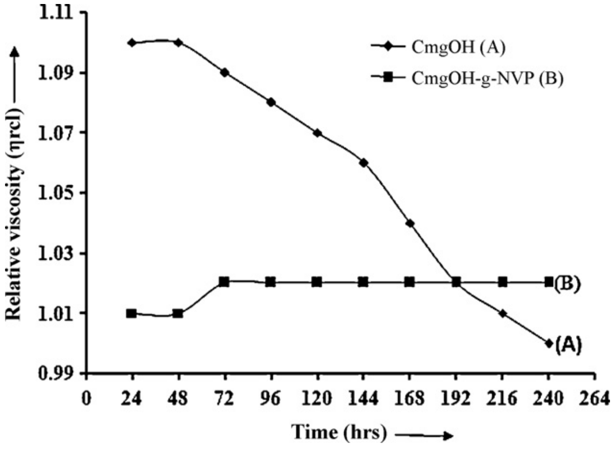


Fig. 5. Resistance to biodegradability.

4. Conclusions

The spectroscopic data confirm that the grafting of N-vinyl-2-pyrrolidone has been taken place on hydroxyl groups of partially carboxymethylated guar gum and this is also supported by tentative mechanism. The thermal analysis data also show that the graft polymer synthesized is more thermally stable than ungrafted polymer, considering both higher final decomposition temperature and integral procedural decomposition temperature as compared to substrate. Grafted polymer (partially carboxymethylated guar gum-g-N-vinyl-2-pyrrolidone) shows very good water swelling ability and resistance to biodegradability and flocculation efficiency.

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