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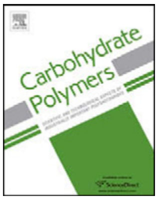

Synthesis of partially hydrolyzed graft copolymer (H-partially carboxymethylated guar gum-g-methacrylic acid): A superabsorbing material

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ABSTRACT

To synthesize a hydrolyzed graft copolymer, the reaction conditions have been optimized to afford maximum grafting followed by maximum absorbency by varying the concentrations of methacrylic acid (from 8×10^{-2} to 24×10^{-2} mol dm^{-3}), potassium peroxymonosulphate (from 0.4×10^{-2} to 2.0×10^{-2} mol dm^{-3}), silver nitrate (from 1.2×10^{-3} to 4.4×10^{-3} mol dm^{-3}), hydrogen ion (from 1.0×10^{-3} to 9.0×10^{-3} mol dm^{-3}) and partially carboxymethylated guar gum (from 0.4 to 1.8 g dm^{-3}) along with N,N′-methylene bisacrylamide (3.0×10^{-3} to 7.0×10^{-3} mol dm^{-3}). The optimum time and temperature for grafting were found to be 40 °C and 120 min, respectively. The saponification reaction of graft copolymer synthesized has been carried out using NaOH (1.5–3.5 N). The effect of methacrylic acid and N,N′-methylene bisacrylamide concentrations on swelling ratio for graft copolymer synthesized i.e. partially hydrolyzed graft copolymer (H-CmgOH-g-MAA) is investigated in water. The graft copolymer is characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis.

1. Introduction

In the present article, modification of partially carboxymethylated guar gum by grafting of vinyl monomers using efficient redox initiators, one of the best and convenient method (Mishra, Tripathy, & Behari, 2008; Mishra, Tripathy, Shrivastava, Mishra, & Behari, 2008; Tripathy, Mishra, & Behari, 2009; Tripathy, Mishra, Yadav, & Behari, 2010) among diverse approaches by means of catalyst such as AIBN (Abdel-Razik, 1997; Egboh, George, & Barrie, 1984) and high energy radiations (Cardona & George, 2002; Dargaville, George, Hill, & Whittaker, 2003; Kabanov & Kudryavtsev, 2003) such as X-ray or gamma-ray are possible for modifying the natural polysaccharides, is performed to impart a desirable and peculiar property like swelling according to the needs of the particular final applications for making superabsorbent polymer material. As superabsorbent hydrogels are mainly hydrophilic polymer networks that swell to a high degree in water or biological fluids due to an extremely high affinity to water (Fujioka, Tanaka, & Yoshimura, 2009; Ramazani-Harandi, Zohuriaan-Mehr, Yousefi, Ershad-Langroudi, & Kabiri, 2006; Wang & Wang, 2009). Hydrogels responding to external stimuli such as heat, pH, electric fields and chemical environments are often referred to as "intelligent" or "smart" hydrogels (Amalia, Rivas, & Riquelme, 2007; Peppas & Mikos, 1986; Takashi, Atsushi, Katsuhiko, & Allan, 2004). These responsive hydrogels have become an important area of research and development in the field of medicine, pharmacy, and biotechnology (Andrade, 1976; Galaev & Mattiasson, 1993; Peppas, 1986; Schacht, 2004). Most hydrogels are formed by copolymerization of different vinyl monomers containing hydrophilic side groups with natural polysaccharides as well as their derivatives (Pourjavadi, Bardajee, & Soleyman, 2009; Pourjavadi, Samadi, & Ghasemzadeh, 2008; Savoji & Pourjavadi, 2006). So that an attempt has been made to synthesis of a new type of unreported graft copolymer (Partially carboxymethylated guar gum-g-methacrylic 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 of 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. Due to 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 derivative find numerous other applications such as in oil industry they act as also major ingredients in drilling muds and fingering fluids whereas in textile industry, help to improve printing quality (Turk & Schneider, 2000). Even though gaur 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) and grafting provides an efficient route not only removing the drawback but also improving its properties towards swelling in various

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solutions. Up to date many investigations have been carried out in view of preparing biopolymer-base advanced materials but reports on grafting onto the partially carboxymethylated guar gum are scantly available in my laboratory (Tripathy, Mishra, Srivastava, Mishra, & Behari 2008; Yadav, Sand, Mishra, & Behari, 2010). So in the light of its versatile applications, this work is carried out with the aim not only to tailor partially carboxymethylated guar gum based hybrid material by grafting of new monomer of methacrylic acid (MAA) but also increasing the application in making super-absorbent polymer of partially carboxymethylated guar gum with methacrylic acid. For this purpose, methacrylic acid has been chosen as monomer, which is hydrophilic in nature (Yamada, Kimura, Tsutaya, & Hirata, 2003). One of the interesting fields of application of poly (methacrylic acid) was in thickening might be used in secondary recovery of petroleum in oil fields, hydraulic fluids and even in liquid rocket-fuels (Jenkins & Hudson, 2002). It also shows adhesive properties that make it useful for the application such as skin protection in medical field (Berger, Reist, Mayer, Felt, & Gurny, 2004). This paper describes synthesis of graft copolymer (partially carboxymethylated guar gum-g-methacrylic acid), as a new hybrid material, which may be used as super absorbent polymeric material.

2. Experimental

2.1. Materials

Partially carboxymethylated guar gum (molecular formula of repeat unit = 598) was received as gift sample from Hindustan gums & Ltd., India. Methacrylic acid (Sigma–Aldrich Co. Ltd., Gillingham, Dorset, UK) was distilled under reduced pressure at 14 mmHg and 55 °C and only middle fraction was used. N,N′-Methylene bisacrylamide as crosslinker and silver nitrate as reductant was received from (E. Merck, India) and used as such respectively. Potassium peroxymonosulphate as an oxidant was received from Du Pont, USA. For maintaining hydrogen ion concentration, sulphuric acid (E. Merck, India) is used. All the solutions were prepared in triple distilled water. The other chemicals used are of analytical grade and used as such without further purification.

2.2. Procedure for graft copolymerization

All the reactions were carried out in three-necked flask under oxygen free nitrogen atmosphere. For each experiment, partially carboxymethylated guar gum (CmgOH) solution has been prepared by adding weighed amount of partially carboxymethylated guar gum (CmgOH) into the reactor containing triple distilled water with rapid stirring. The calculated amount of methacrylic acid and with/without N,N′-methylene bisacrylamide); potassium peroxymonosulphate; silver nitrate and sulphuric acid solutions has been added to the reactor at constant temperature and a slow stream of nitrogen is passed continuously for half an hour, a known amount of deoxygenated potassium peroxymonosulphate solution is added to initiate the reaction. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated out by pouring it into water/methanol mixture ratio (1:5). The grafted sample has been separated by filtration and then dried and weighed. In order to obtain superabsorbent polymer, the sample of graft copolymer is treated with different concentration of NaOH (from 1.5 to 3.5 N) to be alkaline hydrolyzed (Toti & Aminabhavi, 2004).

2.3. Separation of homopolymer

The filtrate has been concentrated by distillation under reduced pressure in the presence of little amount of hydroquinone. The poly methacrylic acid was precipitated by pouring the concentrated filtrate into 5 N H_2SO_4 solution. Poly methacrylic acid thus obtained, has been separated, dried and weighed.

3. Characterization of graft copolymer

3.1. Gravimetric analysis

The grafting parameters have been calculated by using Fanta's expressions (Fanta, 1973a, 1973b).

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

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

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

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

$$\text{Homopolymer} = 100 - \%\text{Grafting effciency}$$

3.2. Instrumental analysis

3.2.1. IR spectroscopy

The IR spectra of partially carboxymethylated guar gum (CmgOH) and grafted samples of partially carboxymethylated guar gum with methacrylic acid (CmgOH-g-MAA) have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1} to provide the proof of the grafting.

3.2.2. Thermo gravimetric analysis

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

4. Study of super absorbency

The swelling of synthesized graft copolymer CmgOH-g-MAA and partially hydrolyzed graft copolymer (H-CmgOH-MAA) has been carried out in triple distilled water. The accurately preweighed samples (0.02 g) of each were immersed in 20 ml of triple distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen samples were then removed from their respective triple distilled water, quickly wiped with filter paper to remove droplets on the surface and weighed. The swelling ratio (S_r) and percent swelling (P_s) have been calculated by using following expressions (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000).

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

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

5. Results and discussions

5.1. Mechanism for grafting and crosslinking reactions

A mechanism has been proposed on the basis of results obtained. Initially silver reacts with potassium peroxymonosulphate under

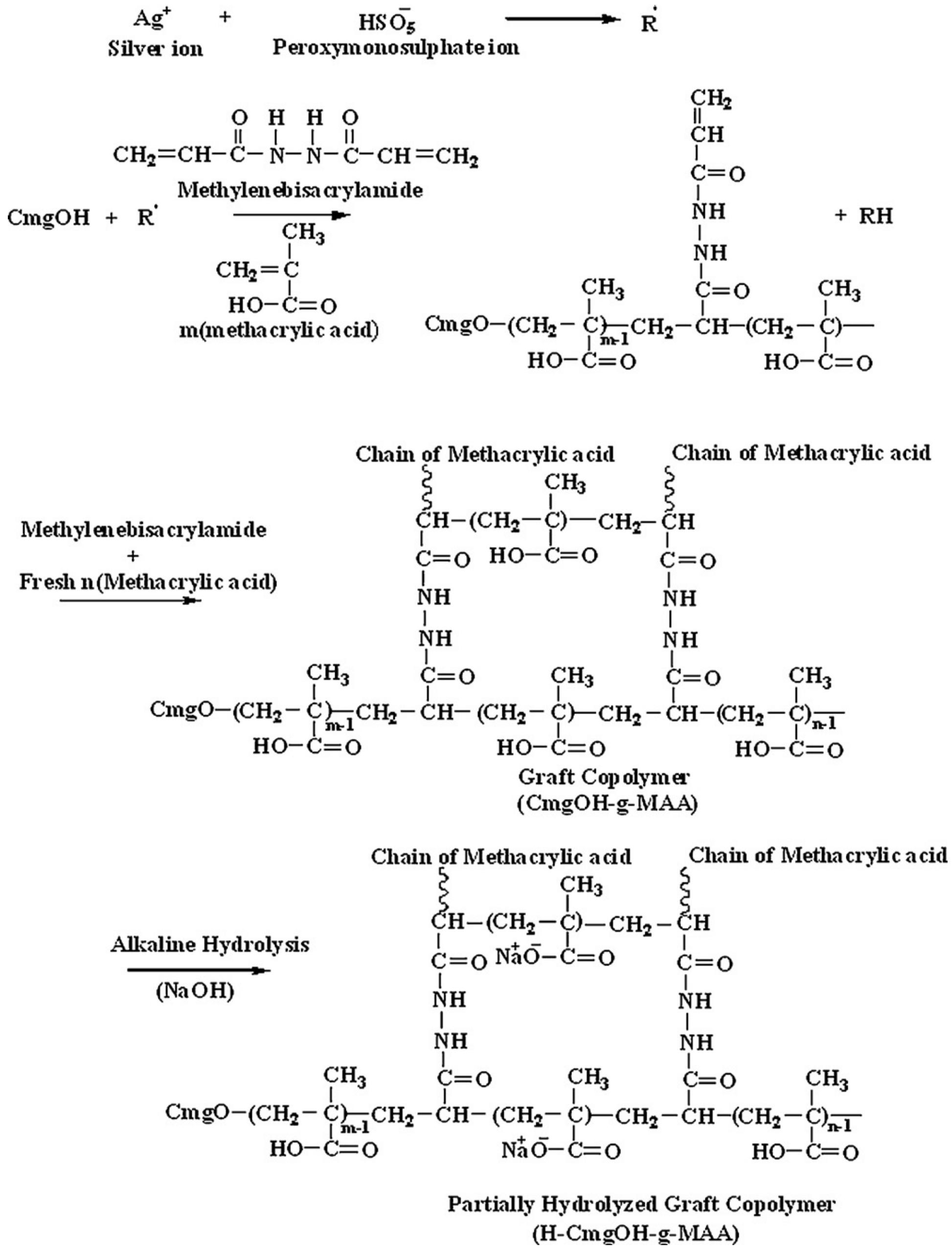

Fig. 1. Reaction scheme for the formation of hydrolyzed graft copolymer (H-CmgOH-g-MAA).

heating to form radicals (Banerjee, Srivastava, Srivastava, & Behari, 2006) represented as $R^\bullet$. The obtained radicals abstract hydrogen atoms from the partially carboxymethylated guar gum (CmgOH) molecules, producing macroradicals of partially carboxymethylated guar gum. The monomer molecules, which are at close vicinity of the reaction sites, become acceptors of partially carboxymethylated guar gum radicals resulting in chain initiation and thereafter themselves become free radical donors to neighbouring molecules. In this way grafted chains grow and terminate by coupling to give graft copolymer. The graft copolymer got crosslinked structure because of the presence of N,N′-methylene bisacrylamide (MBA) as crosslinker in the chemical reaction. The sample of graft copolymer synthesized is treated with NaOH to neutralize (partially/completely) the carboxylic groups of methacrylic acid attached. The mechanism for grafting, alkaline hydrolysis of graft copolymer as well as chemically crosslinking is understood in a reaction scheme given in the form of Fig. 1.

5.2. *Optimization of grafting conditions for maximum absorbency*

In order to obtain graft copolymer as a superabsorbent with water as high as possible, the reaction conditions have been optimized in the case of grafting of methacrylic acid (MAA) with N,N′-methylene bisacrylamide (MBA) onto partially carboxymethylated guar gum. The effect of potassium peroxymonosulphate (PMS) and silver (Ag^+) redox initiators has also been performed in the presence of hydrogen ion (H^+) at constant time and temperature.

5.2.1. *Effect of [methacrylic acid]*

The effect of methacrylic acid (MAA) concentrations on grafting parameters has been investigated by varying the concentrations of methacrylic acid from 8.0×10^{-2} to 24.0×10^{-2} mol dm^{-3}. It has been observed that grafting ratio, add on and efficiency increase continuously (%G = 180.4–254.5, %A = 64.3–74.9, %E = 60.0–71.0) on

Table 1
Effect of [PMS].

[PMS] × 10^2 mol dm^{-3}	%G	%E	%A	%C	%H
0.4	186.4	59.5	65.1	15.5	40.5
0.8	206.4	61.9	67.4	17.0	38.1
1.2	224.5	64.0	69.2	18.2	36.0
1.6	238.4	65.9	70.4	19.0	34.1
2.0	260.4	68.4	72.3	20.4	31.6

[CmgOH] = 1.0 g dm^{-3}, [MAA] = 16 × 10^{-2} mol dm^{-3}, [H^+] = 5 × 10^{-3} mol dm^{-3}, [Ag^+] = 3.2 × 10^{-3} mol dm^{-3}, temperature = 40 °C, time = 120 min.

Table 2
Effect of [silver nitrate].

[Ag^+] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
1.2	160.4	58.7	61.6	12.6	41.3
2.0	188.4	61.3	65.3	15.0	38.7
2.8	224.5	64.0	69.2	18.2	36.0
3.6	250.8	64.8	71.5	20.9	35.2
4.4	320.6	70.3	76.2	25.8	29.7

[CmgOH] = 1.0 g dm^{-3}, [PMS] = 1.2 × 10^{-2} mol dm^{-3}, [MAA] = 16 × 10^{-2} mol dm^{-3}, [H^+] = 5 × 10^{-3} mol dm^{-3}, temperature = 40 °C, time = 120 min.

Table 3
Effect of [H^+] ion.

[H^+] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
1.0	242.6	66.9	70.8	19.0	33.1
3.0	230.4	65.8	69.7	18.3	34.2
5.0	224.5	64.0	69.2	18.2	36.0
7.0	154.6	55.8	60.7	12.9	44.2
9.0	140.8	52.9	58.5	12.1	47.1

[CmgOH] = 1.0 g dm^{-3}, [PMS] = 1.2 × 10^{-2} mol dm^{-3}, [MAA] = 16 × 10^{-2} mol dm^{-3}, [Ag^+] = 3.2 × 10^{-3} mol dm^{-3}, temperature = 40 °C, time = 120 min.

increasing the concentration of methacrylic acid, however, the formation of homopolymer shows a reverse trend (%*H* = 40.0–28.9) with respect to grafting efficiency. This behaviour is attributed due to accumulation of methacrylic molecules to be present in the close proximity of partially carboxymethylated guar gum macroradicals. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of partially carboxymethylated guar gum macroradicals resulting in chain initiation and thereafter themselves become free radical donors to the neighbouring molecules leading lower of termination.

5.2.2. Effect of [PMS]

The effect of potassium peroxymonosulphate on grafting parameters has been studied by varying the concentration of potassium peroxymonosulphate from 0.4 × 10^{-2} to 2.0 × 10^{-2} mol dm^{-3} and the results are summarized in Table 1. The increment in grafting parameters (%*G* = 186.4–260.4, %*A* = 65.1–72.3, %*E* = 59.5–68.4 and %*C* = 15.5–20.4) have been found due to the progressive reduction of potassium peroxymonosulphate by silver ion producing primary free radicals ($OH^\bullet$ and $SO_4{}^{\bullet -}$) which attack on the partially carboxymethylated guar gum molecules, resulting the formation of active sites, on which the addition of methacrylic acid.

5.2.3. Effect of [silver nitrate]

To study the effect of silver nitrate (Ag^+) concentration on grafting parameters, the concentration of silver nitrate has been varied from 1.2 × 10^{-3} to 4.4 × 10^{-3} mol dm^{-3} and the results has been summarized in Table 2. It has been found that grafting ratio, add on, conversion, efficiency and conversion increase continuously (%*G* = 160.4–320.6, %*A* = 61.6–76.2, %*E* = 58.7–70.3 and %*C* = 12.6–25.8) with increase in concentration of silver nitrate. This behaviour might be due to the production of more primary free radicals at faster rate resulting in the production of macroradicals of partial carboxymethylated guar gum.

5.2.4. Effect of [H^+] ion

The effect of hydrogen ion concentration has been studied by varying the concentration from 1.0 × 10^{-3} mol dm^{-3} to 9.0 × 10^{-3} mol dm^{-3} and results are summarized in Table 3. The concentrations of hydrogen ion play an important role during the reaction. The grafting ratio, add on, efficiency, and conversion decreased (%*G* = 242.6–140.8, %*A* = 70.8–58.5, %*E* = 66.9–52.9 and %*C* = 19.0–12.1) with increasing hydrogen ion concentration. With an increase in the hydrogen ion concentration, the concentration of the H_2SO_5 species (Mishra, Tripathy, Srivastava, Pandey, & Behari, 2009) increased, and this resulted in a decrease in the concentration of $HSO_5{}^-$ thereby reducing the grafting parameters.

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

5.2.5. Effect of [CmgOH]

The effect of partially carboxymethylated guar gum (CmgOH) has been observed with an aim to study the effect of its concentration (from 0.4 to 1.8 g dm^{-3}) on grafting parameters. It is obtained that the grafting ratio, add on, efficiency and conversion (%*G* = 180.2–300.5, %*A* = 65.5–75.0, %*E* = 59.9–70.0 and %*C* = 15.8–23.9) increase continuously on increasing the concentration of partially carboxymethylated guar gum (CmgOH). This may be due to greater availability of grafting sites onto partially carboxymethylated guar gum.

5.2.6. Effect of time

To investigate the effect of time on graft copolymerization, the reaction has been carried out by varying the duration of reaction from 60 to 180 min. It has been found that grafting ratio, add on, conversion and efficiency increase (%*G* = 110.2–224.5, %*A* = 52.5–69.2, %*E* = 45.4–64.0 and %*C* = 10.4–18.2) in beginning from 60 to 120 min and thereafter these parameters decrease. This is attributed due to propagation of grafting chains that takes place due to availability of more active species, which accounts for higher grafting. On further increasing the time interval, beyond 120 min, all the active sites get exhausted as the mutual annihilation of growing grafted chains occur, so that grafting parameters decrease (%*G* = 224.5–176.8, %*A* = 69.2–63.9, %*E* = 64.0–59.6 and %*C* = 18.2–14.3).

5.2.7. Effect of temperature

The results, for grafting parameters at different temperatures between 30 °C and 50 °C, are summarized in Table 4. The grafting parameters decrease continuously (%*G* = 280.5–150.6, %*A* = 73.7–60.1, %*E* = 67.7–55.4 and %*C* = 22.8–12.5) with increase in temperature. The decrement in grafting parameters is due to the premature termination of growing grafted chains by excess free radicals at higher temperature.

5.3. IR spectra of partially carboxymethylated guar gum and graft copolymer

IR spectrum of partially carboxymethylated guar gum shows characteristic absorption bands arising from O–H stretching (broad) and C–O stretching near at 3450.0 cm^{-1} and 1023.9 cm^{-1}, respectively. On comparing the spectra of both (presented in the form of Fig. 2), spectrum of graft copolymer (CmgOH-g-MAA) shows variation in intensity and shifting of peak appeared due to O–H stretching from 3450.0 cm^{-1} (broad) to 3447.2 cm^{-1} (sharp) indicating the participation of hydroxyl group in chemical reaction. A characteristic peak, appeared at 1023.9 cm^{-1} in the spectrum of

Table 4
Thermogravimetric analysis.

Sample code	Degradation steps	PDT (°C)	IPDT (°C)	FDT (°C)	T_{max} (°C)
CmgOH	Single	250.0	189.5	900.0	268.8
CmgOH-g-MAA	Four (Quartet)	110.5	247.3	1189.0	248.6, 391.8 783.3, 1032.9

pure partially carboxymethylated guar gum, is also disappeared from the spectrum of graft copolymer. In addition, grafting of methacrylic acid is also confirmed by characteristic absorption bands at 1649.4 cm^{-1} and 1398.3 cm^{-1} due to >C=O stretching and OH bending vibration of carboxylic group of methacrylic acid respectively. A new peak/band at 1109.9 cm^{-1} provides the proof of the presence of ether linkage of backbone with methacrylic acid. The presence of additional peaks/bands in the spectrum of graft copolymer (partially carboxymethylated guar gum-g-methacrylic acid) and disappearance of characteristic peaks/bands from pure partially carboxymethylated guar gum shows that grafting might have been taken place on –OH sites of backbone.

5.4. Thermogravimetric analysis

The data (given in Table 4) of thermogravimetric analysis are obtained from Fig. 3. The curve of partially carboxymethylated guar gum shows single step degradation. The weight loss 1.5% is due to loss absorbed volatile methanol at 54.9 °C. The polymer decomposition temperature has been found at nearly at 250.0 °C. The weight loss increases with increase in temperature from 260.9 °C to 275.2 °C and thereafter decreases and attains maximum at 284.2 °C. T_{max}, the temperature at which maximum degradation occurred is 268.8 °C and final decomposition temperature has been observed at about 900.0 °C. Partially carboxymethylated guar gum-g-methacrylic acid starts to degrade at about 110.5 °C. The rate of weight loss increases with increase in temperature from 110.5 °C to 157.9 °C and thereafter decreases and attains maximum at 283.3 °C. Thus thermal stability of pure partially carboxymethylated guar gum and its graft copolymer (partially carboxymethylated guar gum-g-methacrylic acid) has also been determined by calculating IPDT values using following equation (Doyle, 1961). The area under the curve divided by the total area is the total curve area, A^*, is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, T_{A^*}, by using the equation

$$T_{A^*} = (T_{\mathrm{end}} - T_{\mathrm{initial}})A^* + T_{\mathrm{initial}} \quad (1)$$

where T_{A^*} represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing X-axis up to T_{A^*} and the Y-axis mass fraction remaining at T_{end}. K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in Eq. (1). The integral procedural decomposition temperatures (IPDTs) of pure partially carboxymethylated guar gum and graft copolymer are calculated and found to be 189.5 °C and 247.3 °C, respectively. Thermogravimetric curve of partially carboxymethylated guar gum-g-methacrylic acid also shows four step degradations. First T_{max}, 248.6 °C is due to elimination of absorbed water (moisture). The second T_{max}, i.e. 391.8 °C and third T_{max} i.e. 783.3 °C are due to elimination of $H_3C–CH_3$ and H_2O molecules respectively from pendent chains of methacrylic acid attached to

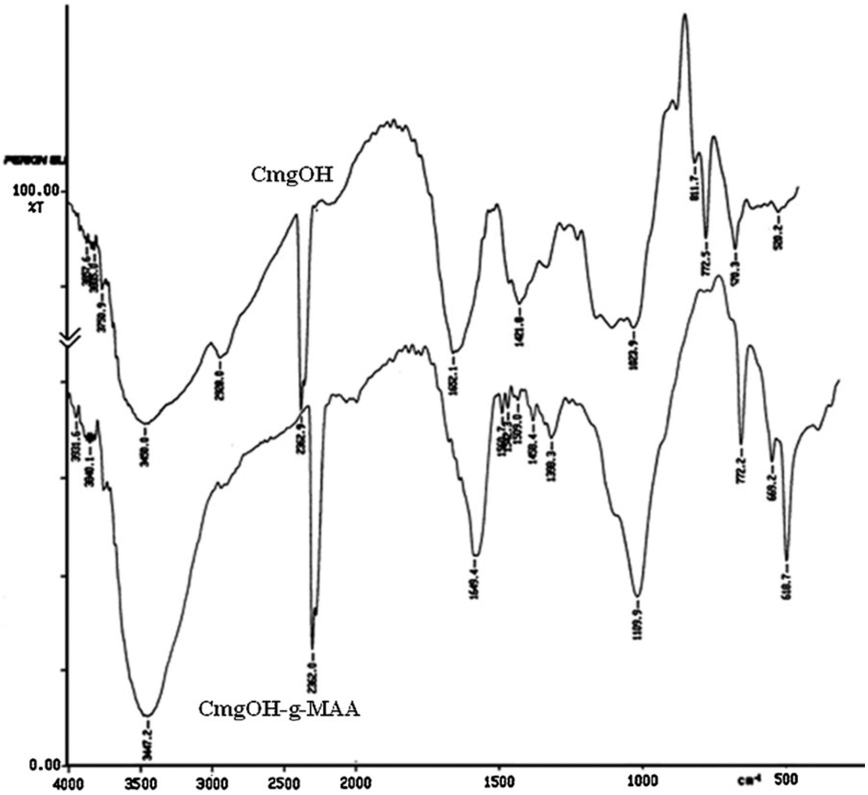

Fig. 2. IR spectra of partially carboxymethylated guar gum (CmgOH) and graft copolymer (CmgOH-g-MAA).

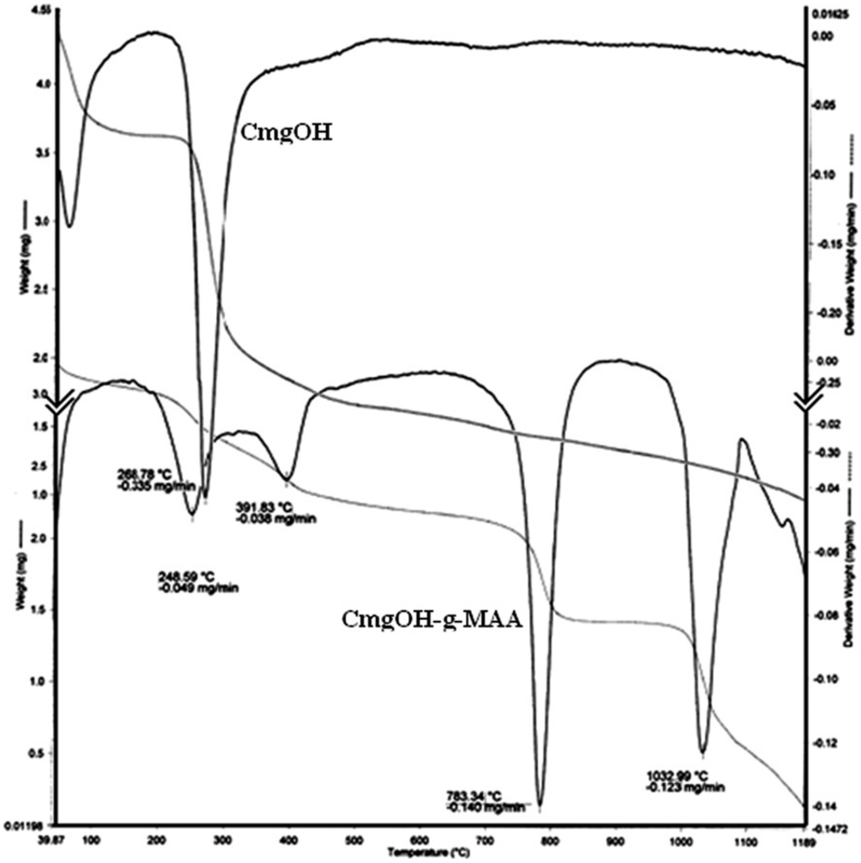

Fig. 3. Thermogravimetric analysis of partially carboxymethylated guar gum (CmgOH) and graft copolymer (CmgOH-g-MAA).

the partially carboxymethylated guar gum. The fourth $T_{\max}$ i.e. 1032.9 °C, is due to the elimination of CO_2 molecule. The final decomposition temperature has been found at about 1189.0 °C. On comparing the thermal analysis of pure partially carboxymethylated guar gum and graft copolymer (partially carboxymethylated guar gum-g-methacrylic acid), it has been observed that integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) of graft copolymer have been found to be higher indicating more stable thermally than pure partially carboxymethylated guar gum.

5.5. *Absorbency of synthesized hydrogel (H-CmgOH-g-MAA)*

The alkaline hydrolysis of graft copolymer (CmgOH-g-MAA) was carried out using different concentrations of NaOH (from 1.5 to 3.5 N) at 50 °C for 120 min. The absorbency was found to be increased initially up to a certain range of sodium hydroxide (from 1.5 to 2.5 N) and then it was decreased with further increase in concentrations of NaOH up to 3.5 N (results presented in Fig. 4A). The initial increment from 120 to 142 in swelling ratio and percent swelling might be attributed to the enhancement of the repulsive action of the increasing carboxylate anions of methacrylic acid attached to the polymeric backbone of partially carboxymethyl guar gum. The higher value of grafting ratio and the grafting efficiency indicates the presence of long chain of methacrylic containing more carboxylate ions. The swelling has been found higher at repulsion of more carboxylate ions occur. The decrement in swelling behaviour (from 142 to 110) might be due to the formation of excess cations, which shield the carboxylate anions and prevent the effective anion–anion repulsion (screening/shielding effect). The screening/shielding effect diminished repulsion and the repulsion leads to a less expanded network of the hydrogel being able retain lower quantities of the aqueous solution. This phenomenon is often referred to as "charge screening effect" (Pourjavadi, Kurdtabar, Mahdavinia, & Hosseinzadeh, 2006).

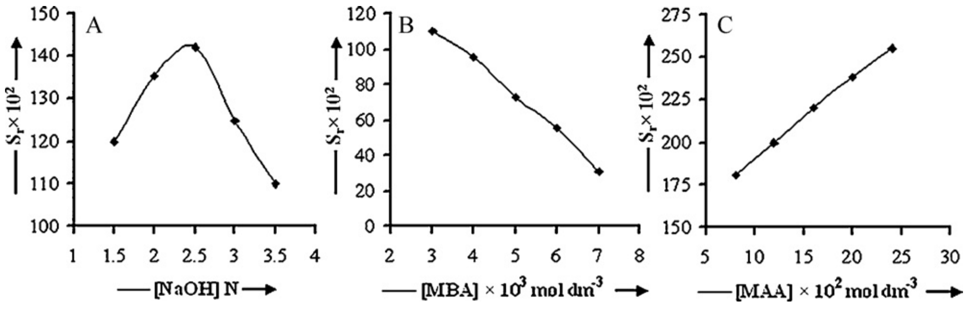

Fig. 4. Effect of NaOH, N,N′-methylene bisacrylamide and methacrylic acid concentrations of swelling ratio.

The effect of crosslinker concentrations on absorbency of partially hydrolyzed graft copolymer (H-CmgOH-g-MAA) product has been shown in Fig. 4B. It has been observed that swelling ratio and percent swelling are decreased continuously (from 110.5 to 30.8) with increase in concentration of crosslinker from 3.0×10^{-3} to 7.0×10^{-3} mol dm^{-3}. This behaviour is due to the higher crosslinking density (Buchholz & Graham, 1997) which causes decrement in space between the chains. The resulting highly crosslinked rigid structure cannot be expanded more and hold a large quantity of water consequently. Such type of behaviour has also been reported by many of the scientists and researchers (Flory, 1953; Peppas & Harland, 1990).

The effect of methacrylic acid concentration on swelling ratio was also studied for the synthesized product (H-CmgOH-g-MAA) and results are presented in Fig. 4C. The absorbency, in terms of percent swelling i.e. from 180.4 to 255.6, increases continuously with increase in concentration of methacrylic acid from 8.0×10^{-2} to 24.0×10^{-2} mol dm^{-3}. The increment in swelling ratio and percent swelling is attributed to the greater availability of methacrylic acid molecules (Athawale & Lele, 1998; Athawale & Vidyagauri, 1998; Lee & Lin, 2001). As the grafting ratio and efficiency increase as the hydrophilicity of monomer increases resulting whole to the hydrogel towards showing maximum absorbency.

6. Conclusion

The spectroscopic data confirm that the grafting of methacrylic acid might have taken place at hydroxyl group presents at partially carboxymethylated guar gum, which is also supported by a tentative reaction scheme. The thermal data show that the synthesized graft copolymer is thermally more stable than pure partially carboxymethylated guar gum. The graft copolymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well industrially. The effects of variables including the concentration of methacrylic acid as well as N,N′-methylene bisacrylamide on swelling ratio has been investigated for the synthesized product i.e. H-CmgOH-g-MAA to show better results and the synthesized hydrogel could be used as a super absorbent material.

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