



Guar gum-g-*N,N'*-dimethylacrylamide: Synthesis, characterization and applications



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ABSTRACT

The graft copolymerization of *N,N'*-dimethylacrylamide onto guar gum initiated by potassium peroxydisulphate/glycolic acid redox pair in an aqueous medium was studied gravimetrically under a nitrogen atmosphere. Grafting ratio, grafting efficiency and add on increase on increasing the concentration of potassium peroxydisulphate (8.0×10^{-3} to 24.0×10^{-3} mol dm $^{-3}$) and glycolic acid concentration (4.4×10^{-3} to 7.6×10^{-3} mol dm $^{-3}$). On increasing the hydrogen ion concentration from 4×10^{-3} to 12.0×10^{-3} mol dm $^{-3}$, grafting ratio, efficiency, add on and conversion were increased. Maximum grafting was obtained when guar gum and *N,N'*-dimethylacrylamide concentration were 1.0×10^{-2} g dm $^{-3}$ and 14.0×10^{-2} mol dm $^{-3}$, respectively. An increase in temperature from 25 °C to 45 °C, the grafting ratio increases but conversion and homopolymer decrease. The optimum time period for graft copolymerization was 2 h. The graft copolymers were characterized by IR spectroscopy and thermogravimetric analysis.

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1. Introduction

Modification of natural polymers by grafting has drawn much attention in recent years (Seaman, 1980). Guar gum, also called guaran, is a galactomannan. It is primarily the ground endosperm of guar beans. It is native to north western parts of India. Chemically, guar gum is a polysaccharide composed of the sugars galactose and mannose. The backbone is a linear chain of 1,4-linked mannose residues to which galactose residues are 1,6-linked at every second mannose, forming short side-branches. It forms colloidal dispersions with water at room temperature and imparts extraordinary viscosity, because of this property, native guar gum as well as its derivatives are commercially impart and find use in such diverse applications like oil well drilling, paper and textile sizing, as a binding agent for explosives, and is widely used in food industry (Sacak & Celik, 1996). Guar gum crosslinked with borax was investigated for water retention applications (Raid, 1985). Although guar gum has wide industrial applications, it suffers from some drawbacks like biodegradability (Wistler, 1973), which limits its uses considerably. These drawbacks can be improved through the grafting of vinyl monomer, which imparts new properties to the polymeric backbone. Grafting provides an efficient route not only removing the drawback but also improving its properties towards swelling and flocculation. Up to date many investigations have been carried

out in view of preparing biopolymer-base advanced materials, but reports on grafting onto the guar gum are scantily available in the light of its versatile applications. This work is carried out with an aim to tailor guar gum based hybrid material by grafting of *N,N'*-dimethylacrylamide (DMA), which is hydrophilic and biocompatible in nature. *N,N'*-dimethylacrylamide is a one of the smart materials that has received considerable attention due to its hydrogel forming property (Aoki et al., 1994; Caykara & Akcakaya, 2006). Because of its hydrophilic (Peppas, 1987) and biocompatible (Kataoka, Miyazaki, Okano, & Sakurai, 1994) nature, it finds numerous applications in the medical and pharmaceutical fields (Berbreiter, Zhang, & Marragnanam, 1993; Liu, Tong, & Yan, 2005) including contact lenses and in drug delivery (De Quieroz, Gallardo, San Roman, & Higa, 1995). Taking in mind all of these fascinating applications of *N,N'*-dimethylacrylamide (DMA) and guar gum, an attempt has been made to graft hitherto unreported *N,N'*-dimethylacrylamide (DMA) onto guar gum. The resulting graft copolymer shows better enhancement in the properties towards water-swelling capacity, metal ion uptake and flocculation than initial polymer.

2. Experimental

2.1. Materials

N,N'-dimethylacrylamide (DMA) (Sigma Aldrich, USA) was distilled under reduce pressure at 14 mm Hg and 55 °C. The only middle fraction was used. Potassium peroxydisulphate (Sigma Aldrich, USA) and Glycolic acid (E. Merck) were used as such. For

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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. Guar gum (GOH) was received as gift sample from Hindustan gums & Chemicals India.

2.2. Procedure of graft copolymerization

The Scheme path way of graft copolymer has been provided in supplementary data. For each experiment guar gum solution was prepared by slow addition of calculated amount of guar gum (0.6×10^{-2} to 1.8×10^{-2} g dm $^{-3}$) into a reactor containing triple distilled water. The calculated amounts of *N,N'*-dimethylacrylamide (6×10^{-2} to 22×10^{-2} mol dm $^{-3}$), sulphuric acid (4×10^{-3} to 12×10^{-3} mol dm $^{-3}$) and glycolic acid (4.4×10^{-3} to 7.6×10^{-3} mol dm $^{-3}$) were added in same reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium peroxy monosulphate solution (8.0×10^{-3} to 24.0×10^{-3} mol dm $^{-3}$) was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen free nitrogen gas. After desired time period the reaction was stopped by letting air into the reactor. The graft copolymer was precipitated by pouring the reaction mixture into water–methanol mixture, so that grafted guar gum was precipitated and poly *N,N'*-dimethylacrylamide remained in the filtrate. The precipitate of grafted guar gum was separated, dried and weighed. To the filtrate a pinch of hydroquinone was added to check the polymerization of unreacted *N,N'*-dimethylacrylamide and concentrated under reduced pressure. The poly *N,N'*-dimethylacrylamide was precipitated by method of [María, Rubio, Dubcovsky, and Navarro \(1997\)](#). Thus poly *N,N'*-dimethylacrylamide obtained was separated, dried and weighed.

2.3. Study of properties

2.3.1. Swelling test

For the swelling studies 0.02 g of each grafted sample, synthesized by varying the concentration of *N,N'*-dimethylacrylamide, has been taken and immersed in 20 ml of triple distilled water and kept undisturbed for 24 h. The surface water on the swollen graft copolymer has been removed by softly pressing it among the folds of filter paper. An increase in weight of graft copolymer has been recorded. Calculation of the percent swelling (P_s) and swelling ratio (S_r) is done by the following expression ([EL-Rehim, EL-Sayed, & Ali, 2000](#)).

$$S_r = \frac{W_2 - W_1}{W_1} \quad (1)$$

$$\text{Percent swelling}(P_s) = \text{Swelling ratio}(S_r) \times 100 \quad (2)$$

where W_1 and W_2 are the mass of sample (g) before and after swelling, respectively.

2.3.2. Metal ion sorption test

The metal ion sorption study has been carried out by using samples of graft copolymers, which have been synthesized by varying the concentration of *N,N'*-dimethylacrylamide from (2.7×10^{-2} to 8.0×10^{-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 guar gum and its grafted polymer (guar gum-g-*N,N'*-dimethylacrylamide) have been determined in terms of different parameters ([Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998](#)), i.e. percent ion uptake (Pu), partition

coefficient (Kd), retention capacity (Qr).

$$\text{Percent uptake(Pu)} = \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion in feed}} \times 100 \quad (3)$$

Partition coefficient(Kd)

$$= \frac{\text{Amount of metal ion in the polymer}}{\text{Amount of metal ion left in the solution}} \times \frac{\text{Volume of solution(ml)}}{\text{Weight of dry polymer}} \quad (4)$$

Retention capacity(Qr)

$$= \frac{\text{Amount of metal ion in the polymer(m Eq.)}}{\text{Weight of dry polymer(g)}} \quad (5)$$

2.3.3. Flocculation test

In 1.0l beaker, 200 ml of 1% (wt/ml) coal suspension in water 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 beaker to make predetermined 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.).

2.4. Characterization

2.4.1. FTIR analysis

The infrared spectra analysis has been utilized 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/DTA analysis

The thermal analysis of guar gum and *N,N'*-dimethylacrylamide grafted guar gum has been carried in inert atmosphere at heating rate of 15 °C per minute up to temperature range of 1400 °C on NETZSCH-STA 409 C/CD thermal analyzer.

3. Results and discussion

3.1. Grafting parameters

The graft copolymer has been characterized according to [Fanta's \(1973a, b\)](#) definition.

$$\text{Grafting ratio}(\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100 \quad (6)$$

$$\text{Grafting efficiency}(\%E) = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100 \quad (7)$$

$$\text{Add on}(\%A) = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100 \quad (8)$$

$$\text{Conversion}(\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100 \quad (9)$$

$$\text{Homopolymer}(\%H) = 100 - \% \text{Grafting efficiency} \quad (10)$$

Table 1
Effect of Variation in precursors on grafting parameters.

Precursors	Variation	%G	%E	%A	%C	%H	Rg $\times 10^6 \text{ mol l}^{-1} \text{ s}^{-1}$
^a [PMS] $\times 10^2 \text{ (mol dm}^{-3}\text{)}$	0.8	84.4	49.8	45.7	12.9	50.2	1.1
	1.2	245.3	67.7	71.0	26.0	32.3	3.4
	1.6	421.0	75.0	80.8	40.4	25.0	5.8
	2.0	484.6	81.8	82.8	42.6	18.2	6.7
	2.4	662.5	84.5	86.8	56.4	15.5	9.2
^b [GA] $\times 10^3 \text{ (mol dm}^{-3}\text{)}$	4.4	398.0	69.6	79.9	41.1	30.4	5.5
	5.2	406.8	72.4	80.2	40.4	27.6	5.6
	6.0	421.0	75.0	80.8	40.4	25.0	5.8
	6.8	378.0	75.7	79.0	35.9	24.3	5.2
	7.6	362.0	73.6	78.3	35.3	26.4	5.0
^c [H ⁺] $\times 10^3 \text{ (mol dm}^{-3}\text{)}$	4.0	386.0	80.4	79.4	34.6	19.6	5.4
	6.0	404.0	77.5	80.1	37.5	22.5	5.6
	8.0	421.0	75.0	80.8	40.4	25.0	5.8
	10.0	356.2	71.6	78.0	35.8	28.4	4.9
	12.0	334.0	69.6	76.9	34.5	30.4	4.6
^d [DMA] $\times 10^2 \text{ (mol dm}^{-3}\text{)}$	6.0	349.2	66.8	77.7	87.8	33.2	4.8
	10.0	376.0	72.4	78.9	52.3	27.6	5.2
	14.0	421.0	75.0	80.8	40.4	25.0	5.8
	18.0	382.0	71.0	79.2	30.1	29.0	5.3
	22.0	340.0	69.5	77.2	22.4	30.5	4.7

^a Effect of potassium peroxymonosulphate concentration.

^b Effect of glycolic acid concentration.

^c Effect of hydrogen ion concentration.

^d Effect of *N,N'*-dimethylacrylamide concentration.

Besides these parameters rate of grafting has also been calculated according to the following formula: [Mohanty & Singh, 1998; Yuan, Sheng, & Shen, 1998; Nayak, Das, & Singh, 1991].

Rate of grafting(Rg)

$$= \frac{\text{Weight of garfted polymer}(W) \times 1000}{\text{Vol.}(V) \times \text{Time}(T) \times \text{molecular weight of DMA}(M)} \text{mol l}^{-1} \text{s}^{-1} \quad (11)$$

where *W* is the weight of grafted guar gum minus weight of pure guar gum; *V*, the volume of the reaction mixture and *T*, the time of reaction in seconds.

3.2. Determination of optimum reaction conditions

The graft copolymerization reaction has been carried out at different concentrations of precursors in order to study their effect on grafting parameters. These precursors are peroxymonosulphate (PMS), glycolic acid (GA), *N,N'*-dimethylacrylamide (DMA), guar gum (GOH) and sulphuric acid (H⁺). The time and temperature were kept constant during reaction.

3.2.1. Effect of peroxymonosulphate concentration

The effect of potassium peroxymonosulphate on graft copolymerisation was studied by varying the concentration from 0.8×10^{-2} to $2.4 \times 10^{-2} \text{ mol dm}^{-3}$. The grafting ratio, add on, efficiency, conversion and rate of grafting have been found to increase continuously on increasing the concentration of PMS from 0.8×10^{-2} to $2.4 \times 10^{-2} \text{ mol dm}^{-3}$ and homopolymer formation decreases (Table 1). The increment in grafting parameters may be due to the progressive reduction of peroxymonosulphate by glycolic acid, which produces more primary free radicals (R[•]) (Mishra, Tripathy, & Behari, 2008) and these primary free radicals generate more active sites on polymeric backbone, to which monomer addition takes place.

3.2.2. Effect of glycolic acid concentration

The effect of variation of glycolic acid on graft copolymerization has been studied by varying its concentration from 4.4×10^{-3} to $7.6 \times 10^{-3} \text{ mol dm}^{-3}$ and results are being summarized in

Table 1. It has been observed that the grafting ratio, efficiency, add on and rate of grafting increase on increasing glycolic acid concentration up to $6.0 \times 10^{-3} \text{ mol dm}^{-3}$ and thereafter grafting ratio, efficiency, add on and rate of grafting decrease whereas homopolymer increases within this concentration range 6.0×10^{-3} to $7.6 \times 10^{-3} \text{ mol dm}^{-3}$. This could be explained due to increase in number of primary free radicals ($\text{CH}(\text{OH})\text{COOH}$, $\text{CH}_2(\text{OH})\text{COO}^\bullet$, $\text{CH}_2(\text{OH})^\bullet$ and $\text{SO}_4^{\bullet-}$), however in high concentration of glycolic acid, i.e. beyond $6.0 \times 10^{-3} \text{ mol dm}^{-3}$, formation of poly *N,N'*-dimethylacrylamide takes place, which decreases grafting efficiency and increases homopolymer percentage.

3.2.3. Effect of concentration of *N,N'*-dimethylacrylamide

The effect of concentration of *N,N'*-dimethylacrylamide on grafting parameters has been investigated by varying the concentration of *N,N'*-dimethylacrylamide from 6.0×10^{-2} to $22.0 \times 10^{-2} \text{ mol dm}^{-3}$ and results are presented in Table 1. It has been observed that grafting ratio, add on, efficiency and rate of grafting increase on increasing the concentration up to $14 \times 10^{-2} \text{ mol dm}^{-3}$ and thereafter, grafting parameters decrease. However the formation of homopolymer shows a reverse trend with respect to grafting efficiency. This behaviour 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 guar gum radicals resulting in chain initiation and according themselves become free radical donor to the neighbouring molecules. But on further increasing the concentration of *N,N'*-dimethylacrylamide, decrease in grafting parameter is observed which is due to viscosity increase of the medium, which in turn hinders the movement of free radicals.

3.2.4. Effect of sulphuric acid concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the reaction has been carried out at various concentration of sulphuric acid, i.e. from 4.0×10^{-3} to $12.0 \times 10^{-3} \text{ mol dm}^{-3}$ and results have been presented in Table 1. It has been found that the grafting ratio, add on, efficiency and rate of grafting increase on increasing the concentration of hydrogen ion up to $8.0 \times 10^{-3} \text{ mol dm}^{-3}$. However, beyond this concentration

grafting ratio, add on, efficiency, conversion and rate of grafting decrease while homopolymer increases. This behaviour might be due to the formation of H_2SO_4 inactive species, thus the concentration of HSO_5^- decreased resulting in less production of primary free radicals, which is responsible for the graft copolymerization thereby decreasing the grafting parameters.

3.2.5. Effect of guar gum concentration

The effect of guar gum concentration on grafting parameters has been studied by varying the concentration of guar gum from 0.6 to 1.8 g dm^{-3} . As the concentration of guar gum increased from 0.6 to 1.0 g dm^{-3} grafting ratio (%G = 356–421), add on (%A = 78–80), and efficiency increase (%E = 56–75). This could be due to availability of more grafting sites with increasing concentration of guar gum. As the concentration of guar gum further increase beyond 1.0 g dm^{-3} the viscosity of reaction medium increases which hinders the movement of *N,N'*-dimethylacrylamide and guar gum macro radicals thereby decreasing the grafting parameters (%G = 421–324, %A = 80–76, %E = 75–71).

3.2.6. Effect of time period

The effect of reaction time was studied by changing the time period of reaction from 90 to 180 min. An increase in the grafting ratio (%G = 264–421), efficiency (%E = 65–75), add on (%A = 72–80) and conversion (%C = 29–40) with increasing time period from 90 min to 120 min was observed. Beyond this time period grafting ratio, efficiency, conversion and add on decreased (%G = 421–283, %E = 75–64, %C = 40–31, %A = 80–73), where homopolymer (%H = 25–36)) was found to increase. With increasing the time period propagation of grafting chains takes place due to availability of more active species, which accounts for higher grafting. Further increase in time interval the mutual annihilation of growing grafted chains occurred, which resulted the decrease in grafting ratio, add on, efficiency and increase in homopolymer formation.

3.2.7. Effect of temperature

It was observed that as the temperature was increased from 25 to 35°C , grafting parameters, i.e. grafting ratio (%G = 343–421), efficiency (%E = 68–75) and add on increased (%A = 77–80) it might be due to production of more free radicals causing an increase in these parameters. On further increasing temperature the grafting parameters showed decreasing (%G = 421–345, %E = 75–65, %C = 40–37, %A = 80–77) trend because at higher temperature potassium peroxy monosulphate decomposed to give HSO_4^- , H_2O , O_2 as reported (Cotton & Wilkinson, 1976). Since O_2 acts as a scavenger for free radicals, decreasing the concentration of all types of radicals.

3.3. Evidence of grafting

3.3.1. IR spectra of guar gum and guar gum-g-*N,N'*-dimethylacrylamide

The IR spectra of samples in KBr pellets were recorded using a Perkin Elmer FTIR spectrophotometer (PARAGON 1000) in the range $450\text{--}4000 \text{ cm}^{-1}$. IR spectrum of guar gum (Fig. 1) shows characteristic absorption bands arising from —OH stretching (broad) near 3019.97 cm^{-1} . On comparing the spectra of both, guar gum and its graft copolymer, GOH-g-DMA (Fig. 2) shows a sharp band at 3620.36 cm^{-1} . The sharpness of band indicates the participation of hydroxyl groups in chemical reaction. The attachment of DMA is also further confirmed by the appearance of additional characteristic absorption bands at 1602.61 and 1406.0 cm^{-1} due to C=O stretching vibration and C—N stretching vibration of tertiary amide of DMA, respectively. The presence of additional peaks/bands in the spectrum of GOH-g-DMA also shows that grafting might have been taken place on OH sites of backbone.

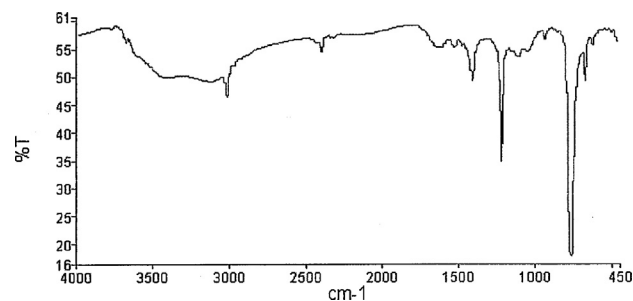


Fig. 1. IR spectrum of guar gum.

3.3.2. Thermogravimetric analysis of guar gum and guar gum-g-*N,N'*-dimethylacrylamide

The integral procedural decomposition temperature (IPDT) accounts for the whole shape of the thermogravimetric curve in a single number by measuring the area under the curve. Proposed by Doyle (1961), the IPDT has been correlated to volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials (Vyazovkin & Sbirrazzuoli, 2006). IPDT was calculated using the following equations:

$$\text{IPDT}(^\circ\text{C}) = A^*K^*(T_f - T_i) + T_i \quad (12)$$

$$A^* = S_1 + S_2/S_1 + S_2 + S_3 \quad (13)$$

$$K^* = S_1 + S_2/S_1 \quad (14)$$

where A^* is the area ratio of the total experimental curve defined by the total TGA thermogram, T_i is the initial experimental temperature, and T_f is the final experimental temperature. S_1 , S_2 , and S_3 values for calculating A^* and K^* are given in a reported work (Yadav, Sand, & Behari, 2012). Thermogravimetric analysis curve (presented in Fig. 3) of guar gum shows single step degradation. The 4.26 weight loss at 59°C might be due to loss of absorbed methanol (Fig. 3). It starts to degrade at 100.0°C . The polymer decomposition temperature (PDT) has been found at 285°C . The rate of weight loss increases with increase in temperature from 200°C to 236°C and thereafter decreases and attains a maximum value at about 300°C . T_{max} , temperature at which maximum degradation occurred, is 300°C which is also confirmed by the peak appeared at about 299°C in DTA curve of guar gum (presented in Fig. 3). The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at 385°C and 447°C , respectively. In case of guar gum-g-*N,N'*-dimethylacrylamide the weight loss 5.69 mg at about 100°C might be due to loss of absorbed water (Fig. 4). The polymer decomposition temperature (PDT) has been found at 157°C . It has been found that degradation of guar gum-g-*N,N'*-dimethylacrylamide starts at about 140°C temperature. The rate of weight loss increases with increase in temperature from 245°C to 300°C and there after decreases and attains maximum

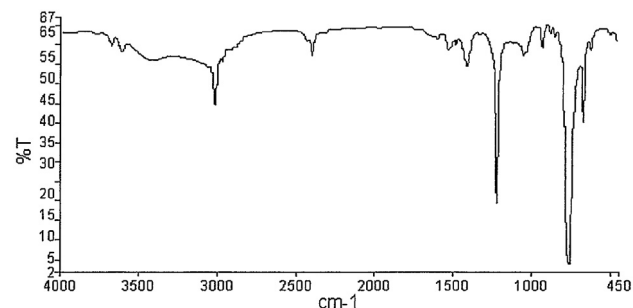


Fig. 2. IR spectrum of guar gum-g-*N,N'*-dimethylacrylamide.

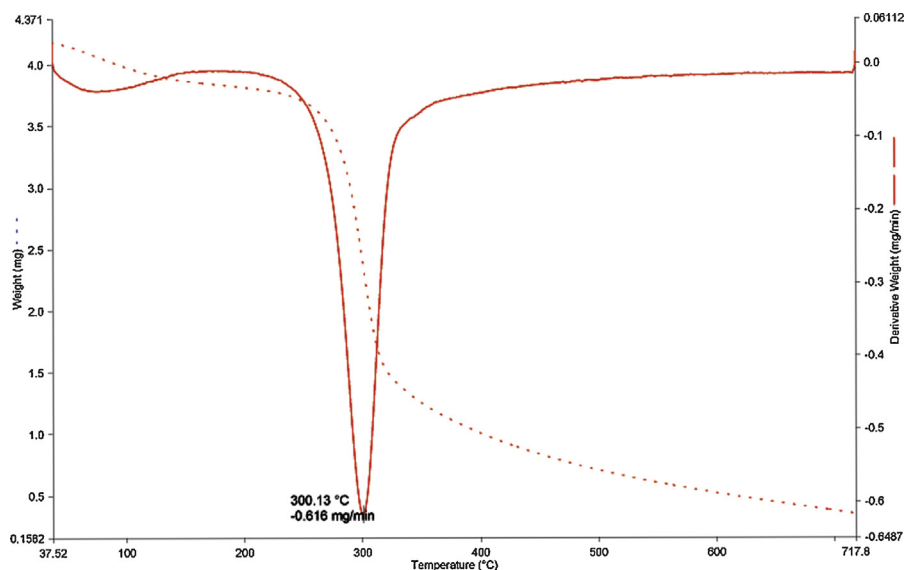
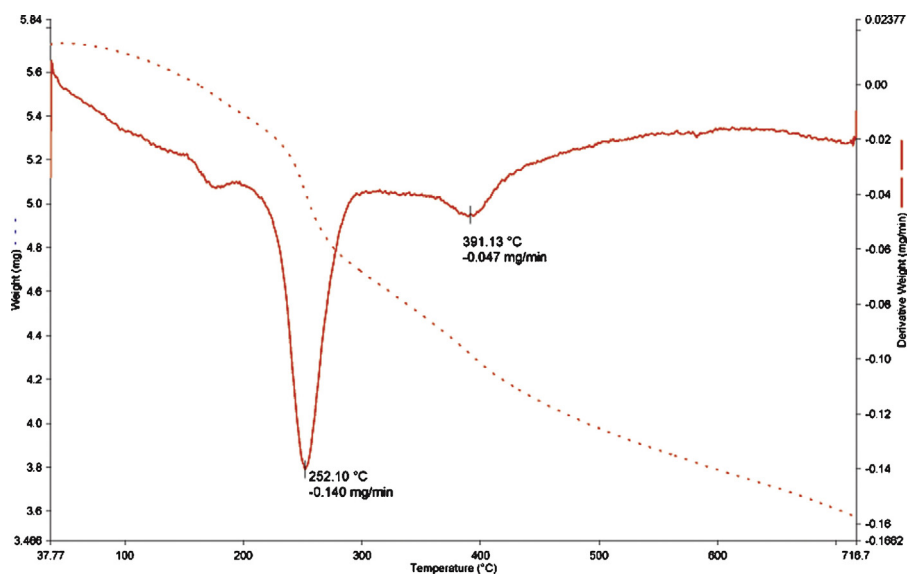


Fig. 3. Thermogravimetric trace of guar gum.

Fig. 4. Thermogravimetric trace of guar gum-g-*N,N'*-dimethylacrylamide.

at about 221 °C. Guar gum-g-*N,N'*-dimethylacrylamide shows two step degradation. First and second $T_{\max}$ has been found at 252 °C and 391 °C, respectively. The integral procedural decomposition (IPDT) and final decomposition temperature (FDT) have been found at about 646 °C and 800 °C, respectively. On comparing the thermograms of parent backbone (guar gum) and graft copolymer (guar gum-g-*N,N'*-dimethylacrylamide), it has been observed that final and integral procedural decomposition have been found to be higher for graft copolymer. This indicates that graftcopolymer is thermally stable than backbone.

3.4. Properties

3.4.1. Swelling studies

An increase in weight of graft copolymer has been recorded by performing swelling test. The results have been summarized in Table 2, which indicates that swelling ratio and swelling percent depend on the concentration of monomer used while grafting. Since *N,N'*-dimethylacrylamide is a hydrophilic monomer, it increases the water retention capacity of graft copolymer. On

increasing the concentration of *N,N'*-dimethylacrylamide, grafting is increased, which may result into coiling network of poly (*N,N'*-dimethylacrylamide), thus imbibes more water. The presence of amide group of substrate and a hydrophilic monomer, both factors are responsible for good swelling capacity of graft copolymer. Swelling percent is increased with increased percent grafting because on increasing *N,N'*-dimethylacrylamide concentration,

Table 2

Swelling capacity of graft copolymer (GOH-g-DMA).

Sample code	[DMA] $\times 10^2$ mol dm $^{-3}$	%G	P_S	S_R
A	6.0	349.2	165	1.65
B	10.0	376.0	190	1.9
C	14.0	421.0	270	2.7
D	18.0	382.0	150	1.5
E	22.0	340.0	120	1.2

^aSwelling capacity of graftcopolymer (GOH-g-DMA): [GOH] = 1.0 g dm $^{-3}$; [H $^+$] = 8×10^{-3} mol dm $^{-3}$; Time = 120 min; [PMS] = 1.6×10^{-2} mol dm $^{-3}$; Temp = 35 °C; [GA] = 6.0×10^{-3} mol dm $^{-3}$.

A, B, C, D, and E indicates the sample of graft copolymer.

Table 3
Metal ion sorption.

Sample	[DMA] $\times 10^2$ mol dm ⁻³	%G	Percent uptake (Pu)			Partition coefficient (Kd)			Retention capacity (Qr)		
			Pb ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺
GOH			3.1	5.1	4.3	16.4	24.1	19.5	2.8	3.5	3.2
A	6.0	349.2	5.13	4.14	3.41	13.52	10.35	8.83	3.8	4.8	4.0
B	10.0	376.0	6.65	5.60	4.45	17.83	14.84	11.6	4.5	5.7	5.6
C	14.0	421.0	11.23	10.66	9.34	31.64	29.85	25.7	7.1	6.2	5.8
D	18.0	382.0	9.43	9.58	7.56	26.03	26.5	20.4	6.0	7.0	6.0
E	22.0	340.0	7.76	7.05	5.78	21.05	18.96	15.3	5.6	6.0	5.9

Metal ion sorption: [GOH] = 1.0 g dm⁻³; [PMS] = 1.6×10^{-2} mol dm⁻³; Time = 2 h; [H⁺] = 8×10^{-3} mol dm⁻³; Temp = 35 °C; [GA] = 6.0×10^{-3} mol dm⁻³.
GOH = Guar gum and A, B, C, D, E indicates the sample of graft copolymer.

pendant chain of poly (*N,N'*-dimethylacrylamide) grows thereby increasing the swelling capacity of graft copolymer.

3.4.2. Metal ion sorption behaviour of guar gum and its graft copolymer

The results, as summarized in Table 3, of sorption behaviour of both guar gum and its graft copolymer (guar gum-*g-N,N'*-dimethylacrylamide) have been determined. It has been observed that the values of percent ion uptake (Pu), partition coefficient (Kd) and retention capacity (Qr) 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 due to availability of additional functional groups of monomer grafted, i.e. *N,N'*-dimethylacrylamide and increment in sorption capacity takes place due to the incorporation of its pendant chain of poly (*N,N'*-dimethylacrylamide), so higher the grafting, higher will be the sorption of metal ion. Results also show that Pb²⁺ was least uptakable in comparison to two metal ions, which have been used. A scheme of metal ion uptake of graft copolymer has been published in our previous research paper (Srivastava, Mishra, & Behari, 2010).

3.4.3. Flocculation performance

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 guar gum and graft copolymer of guar gum with *N,N'*-dimethylacrylamide. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in Fig. 5.

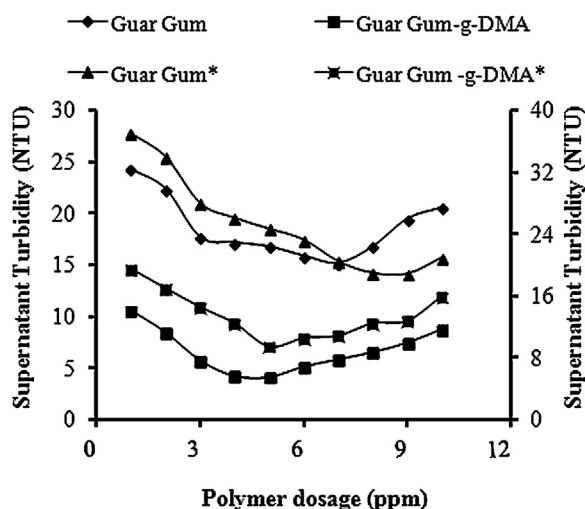


Fig. 5. Effect of polymer dosage on turbidity for coking coal and non-coking coal*.

It has been found that grafted copolymer (guar gum-*g-N,N'*-dimethylacrylamide) shows better performance than guar gum itself which could be explained due to the fact that in grafted copolymer, the dangling of poly(*N,N'*-dimethylacrylamide) chains have better approachability (Deshmukh, Singh, & Chaturvedi, 1985) to the contaminant coal particles (Bratby, 1980). Here the bridging mechanism operates (Gregory, 1982), which involves binding or bridging individual particles to form flocs, hence increases its flocculation capability. By grafting of poly *N,N'*-dimethylacrylamide onto guar gum, efficient flocculant has been obtained.

4. Conclusions

The spectroscopic data confirm that the grafting of *N,N'*-dimethylacrylamide might have taken place at hydroxyl groups of guar gum, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that the graft copolymer synthesized is thermally more stable than guar gum. The graft copolymer synthesized, i.e. guar gum-*g-N,N'*-dimethylacrylamide also shows enhancement in the physicochemical properties studied in terms of swelling, metal ion sorption, flocculation. Thus, it could be concluded that the graft copolymer 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.2013.08.024>.

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