



Synthesis, characterization and applications of graft copolymer (Chitosan-g-*N,N*-dimethylacrylamide)

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ARTICLE INFO

Article history:

Received 7 May 2009

Received in revised form 24 June 2009

Accepted 10 July 2009

Available online 16 July 2009

Keywords:

Graft copolymer

Potassium peroxymonosulphate

Mandelic acid

FTIR spectroscopy

Thermal analysis

ABSTRACT

An unreported graft copolymer of *N,N*-dimethylacrylamide (DMA) with chitosan has been synthesized under nitrogen atmosphere using peroxymonosulphate/mandelic acid redox pair. The effect of reaction conditions on grafting parameters i.e. grafting ratio, efficiency, conversion, add on and homopolymer has been studied. Experimental results show that maximum grafting has been obtained at 1.0 g dm^{-3} concentration of chitosan, $30 \times 10^{-2} \text{ mol dm}^{-3}$ concentration of *N,N*-dimethylacrylamide and $7.0 \times 10^{-3} \text{ mol dm}^{-3}$ concentration of hydrogen ion. It has also been observed that grafting ratio, add on, conversion and efficiency increase upto $3.2 \times 10^{-3} \text{ mol dm}^{-3}$ of mandelic acid, $12.0 \times 10^{-3} \text{ mol dm}^{-3}$ of potassium peroxymonosulphate, 150 min of time and 40°C of temperature. Grafted polymer has been characterized by FTIR spectroscopy and thermogravimetric analysis. Water swelling capacity of chitosan-g-*N,N*-dimethylacrylamide has been determined. It has been observed that the graft copolymer is thermally more stable than parent backbone.

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1. Introduction

Chitosan is a unique basic polysaccharide obtained by *N*-deacetylation (Dambies, Guimon, Yiacoumi, & Guibal, 2001; Sashiwa, 2005; Verma et al., 2005) of chitin in alkaline medium, which consists mainly of β -(1 \rightarrow 4)-2-acetamido-2-deoxy-D-glucose units and is the second most abundant biopolymer on Earth after cellulose, widely distributed in crustacean shells and cell walls of fungus (eubacteria and various mushrooms) (Dutta, Dutta, Chattopadhyaya, & Tripathi, 2004; Mathur & Narang, 1990). Owing to its toxicity (Park, Park, & Kim, 2006), biocompatibility (Dutta, Ravikumar, & Dutta, 2002; Ravi Kumar, 2000) and non-carcinogenicity (Muzzarelli, 1997) along with the presence of reactive and functional groups, chitosan finds many perspective applications in flocculation, waste water treatment etc. (Hejazi & Amiji, 2003; Jayakumar, Prabahara, Reis, & Mano, 2005; Takayama et al., 1990). Despite of various applications, poor solubility of chitosan in common organic solvents and its susceptibility for microbial attack restricts its widespread industrial exploitation. Now days, a lot of attention has been paid on chemical modification of chitosan, which offers a new route for enhancing the potential abilities. Of all possible modifications, graft copolymerization of vinyl monomers onto natural polysaccharides (Srivastava, Tripathy, Mishra, & Behari, 2007; Tripathy, Mishra, Mishra, & Behari, 2008) is quite promising. Grafting onto chitosan and its derivatives has been the thrust of researchers (Caner, Hasipoglu, Yilmaaz, & Yilmaaz,

1998; Pedram & Retuert, 1998; Shantha, Bala, & Rao, 1995; Sun, Xie, & Xu, 2004). In chitosan, both hydroxyl and amino groups are possible sites for the reaction to incorporate new and desired functional groups thus could be designed into a hybrid product keeping the main skeleton intact. Recently workers have also been explored as excipients in drug delivery (Mullarney, Seery, & Weiss, 2006). *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 and biocompatible (Peppas, 1987) 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 Queriros, Gallardo, San Roman, & Higa, 1995). This paper deals the synthesis of chitosan grafted *N,N*-dimethylacrylamide using potassium peroxymonosulphate/mandelic acid redox pair with an aim to develop a hybrid product which could be used for specialty uses such as in waste water treatment. The effect of reaction conditions on grafting parameters has been studied to obtain the optimum reaction conditions. Swelling capacity of grafted chitosan has also been investigated.

2. Experimental

2.1. Materials

N,N-dimethylacrylamide (DMA) (Sigma-Aldrich, USA) was distilled at 11 mm mercury pressure at 48°C and only middle fraction

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was used. Potassium peroxymonosulphate (Sigma–Aldrich, USA), mandelic acid (E. Merck, India) and acetic acid (E. Merck, India) were used as such. Chitosan was purchased from Aldrich. Acetic acid (E. Merck, India) was used. While, sulphuric acid (E. Merck, India) has been used as a source for hydrogen ion and all the solutions were prepared in triple distilled water. Other reagents are of analytical grade. For the flocculation, coking and non-coking coals used were received from steel plant Bokaro, India.

2.2. Procedure for grafting

For each experiment chitosan solution was prepared by dissolving it in acetic acid as reported in literature (Gupta & Ravi Kumar, 2000). A calculated amount of chitosan, *N,N*-dimethylacrylamide, sulphuric acid and mandelic acid were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min at constant temperature. 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. After desired time period, the reaction was stopped by letting air into reactor. The reaction mixture was poured in a water methanol mixture (ratio 1:5). Thus grafted material precipitated which was separated, dried and weighed. The poly *N,N*-dimethylacrylamide remained in the filtrate. To the filtrate a pinch of hydroquinone was added and concentrated by distillation under reduced pressure. The polymer of *N,N*-dimethylacrylamide was precipitated by pouring it into pure methanol. The poly *N,N*-dimethylacrylamide thus 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 between 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 Abd, Hegazy El-Sayed, & Ali, 2000).

$$P_s = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}} \times 100$$

$$S_R = \frac{\text{Wt. of swollen polymer} - \text{Wt. of dry polymer}}{\text{Wt. of dry polymer}}$$

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 $14.0 \times 10^{-2} \text{ mol dm}^{-3}$ to $30.0 \times 10^{-2} \text{ mol dm}^{-3}$. 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 chitosan and its grafted polymer with *N,N*-dimethylacrylamide has been determined in terms of different parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998) i.e. percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r).

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

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

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

2.3.3. Flocculation test

In 1.0 l beaker, 200 ml of 1%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 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.).

2.4. 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 $500\text{--}4000 \text{ cm}^{-1}$.

2.4.2. TGA/DTA analysis

The thermal analysis of chitosan and *N,N*-dimethylacrylamide grafted chitosan 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 (Fanta, 1973) definition.

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

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

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

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

$$\text{Homopolymer } (\%H) = 100 - \%E$$

3.2. Determination of optimum reaction conditions

The graft copolymerization reaction has been carried out at different concentration of reactants in order to study their effect on grafting parameters. The reactants are potassium peroxymonosulphate (PMS), mandelic acid (MA), *N,N*-dimethylacrylamide (DMA), chitosan (ChXH), sulphuric acid along with the temperature and time period.

3.2.1. Effect of potassium peroxymonosulphate concentration

The effect of potassium peroxymonopersulphate on grafting reaction has been studied and results are given in Table 1. The grafting ratio, add on, efficiency and conversion have been found to increase on increasing the concentration of potassium peroxymonopersulphate (PMS) from 6×10^{-3} to 12×10^{-3} mol dm $^{-3}$ and homopolymer formation decreases within this concentration range however after this concentration, there is decrement in grafting parameters. The increment in grafting parameters from 6×10^{-3} to 12×10^{-3} mol dm $^{-3}$ could be explained due to the progressive reduction of PMS by mandelic acid producing MA $^{\circ}$ and $\dot{\text{O}}\text{H}$ as reactive species, which interact with *N,N*-dimethylacrylamide and chitosan molecules to produce free radicals, which propagate the growing grafted chains giving rise to increment in grafting parameters. Beyond 12×10^{-3} mol dm $^{-3}$, the grafting parameters decrease, which may be attributed due to premature termination of growing grafted chains.

3.2.2. Effect of mandelic acid concentration

The results obtained by variation of concentration of mandelic acid (MA) which reveals that the grafting ratio (%G = increases from 81.0 to 192.5), add on, efficiency and conversion increase on increasing the concentration of mandelic acid from 1.6×10^{-3} to 3.2×10^{-3} mol dm $^{-3}$ but beyond this concentration range, grafting parameters decrease (%G = decreases from 192.5 to 102.7), however, homopolymer increase. The increase in grafting parameters is attributed due to increase in number of primary free radicals (MA $^{\circ}$ and $\dot{\text{O}}\text{H}$), but at high concentration of mandelic acid i.e. beyond 3.2×10^{-3} mol dm $^{-3}$, the decrement in grafting parameters is probably due to premature termination of *N,N*-dimethylacrylamide radicals giving rise to more homopolymer.

3.2.3. Effect of hydrogen ion concentration

The effect of concentration of hydrogen has been studied by varying the concentration of sulphuric acid from 3.0×10^{-3} mol dm $^{-3}$ to 11.0×10^{-3} mol dm $^{-3}$. The grafting parameters have been found to decrease by increasing the hydrogen ion concentration within the cited range. This behaviour could be explained by the fact that on increasing the hydrogen ion concentration formation of H $_2$ SO $_5$ as an inactive species increases, due to which concentration of HSO $_5^-$ decreases resulting in production of less free radicals, thereby decreasing the grafting parameters (%G = decreases from 243 to 105.6).

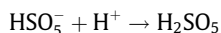


Table 1

Effect of peroxymonosulphate concentration. [DMA] = 22.0×10^{-2} mol dm $^{-3}$, [ChXH] = 1.0 g dm $^{-3}$, [MA] = 3.2×10^{-3} mol dm $^{-3}$, [H $^+$] = 7×10^{-3} mol dm $^{-3}$, temp. = 35 °C, time = 120 min.

[PMS] $\times 10^3$ mol dm $^{-3}$	%G	%E	%A	%C	%H
6	124.7	72.5	55.4	7.8	27.5
8	151.2	78.3	60.2	10.1	21.7
10	192.5	81.4	65.8	10.9	18.6
12	215.3	86.5	68.3	11.4	13.5
14	243.3	89.0	70.9	12.1	11.0

Table 2

Effect of *N,N*-dimethylacrylamide concentration. [ChXH] = 1.0 g dm $^{-3}$, [PMS] = 10×10^{-3} mol dm $^{-3}$, [MA] = 3.2×10^{-3} mol dm $^{-3}$, [H $^+$] = 7×10^{-3} mol dm $^{-3}$, temp. = 35 °C, time = 120 min.

[DMA] $\times 10^2$ mol dm $^{-3}$	%G	%E	%A	%C	%H
14	136.2	72.0	57.7	13.6	27.9
18	168.0	76.6	62.7	12.3	23.4
22	192.5	81.4	65.8	10.8	18.6
26	220.3	85.1	68.8	10.0	14.9
30	254.3	89.3	71.8	9.6	10.7

3.2.4. Effect of *N,N*-dimethylacrylamide concentration

The effect of *N,N*-dimethylacrylamide concentration on grafting parameters has been studied by varying its concentration from 14.0×10^{-2} to 30.0×10^{-2} mol dm $^{-3}$ and results (in Table 2) show that grafting parameters increase on increasing the concentration of *N,N*-dimethylacrylamide (DMA). However, the formation of homopolymer and conversion show a reverse trend with respect to grafting efficiency. The increase in grafting parameters might be attributed due to accumulation 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 chitosan macroradicals resulting in chain initiation and thereafter themselves becomes free radical donor to neighbouring molecules causing the lowering of termination.

3.2.5. Effect of chitosan concentration

To examine the effect of chitosan concentration on grafting parameters, its concentration has been varied from 0.6 to 1.4 g dm $^{-3}$. The grafting ratio, add on, conversion increase on increasing the concentration of chitosan up to 0.8 g dm $^{-3}$ and homopolymer formation decreases, but beyond this concentration range, grafting parameters decrease (Fig. 1). The increment in grafting parameters up to certain concentration range could be explained due to the availability of more grafting sites with increasing concentration of chitosan, however on further increasing the concentration beyond 0.8 g dm $^{-3}$, the viscosity of the medium increases, which hinders the movement of free radicals thereby decreasing the grafting parameters.

3.2.6. Effect of time period

The grafting reaction has been carried out for different intervals of time to study the effect of time period on reaction. Grafting ratio (%G = increases from 93.3 to 235.6), efficiency and add on increase on increasing the time period from 60 to 150 min. On further increment in time period grafting parameters show decreasing trend (up to %G = 92.9). This behaviour may be explained on the basis that as the reaction progresses and time increases, the amount of graft copolymer increases due to availability of more active species, which give low percentage of homopolymer. But beyond the reaction time of 150 min, termination of growing grafted chain takes place at faster rate, thus decrement in grafting parameters is observed.

3.2.7. Effect of temperature

It has been found that grafting ratio, add on, conversion and efficiency increase as temperature increases from 25 to 40 °C, but thereafter the values of these parameters are found to decrease

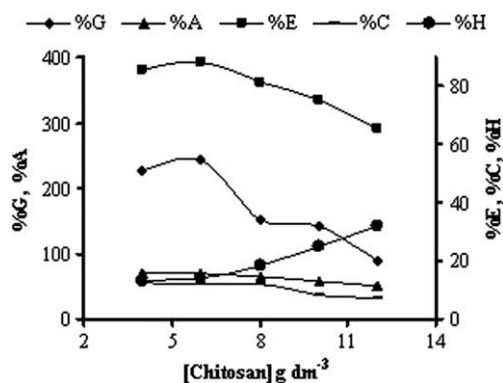
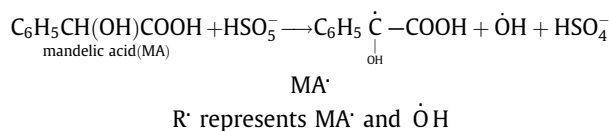


Fig. 1. Effect of chitosan. [DMA] = 22×10^{-2} mol dm $^{-3}$, [H $^+$] = 7×10^{-3} mol dm $^{-3}$, [PMS] = 10×10^{-3} mol dm $^{-3}$, [MA] = 3.2×10^{-3} mol dm $^{-3}$, temp. = 35 °C, time = 120 min.

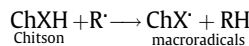
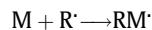
(Table 3). The increase in the values of grafting parameter may be attributed due to the fact that with increase in temperature, rate of production of primary free radicals increase, causing an increase in value of grafting parameters. However, further, increase in temperature that is above 40 °C, there is decrease in grafting parameters, which might be due to destruction of primary free radicals due to effective collisions at higher temperature.

3.3. Mechanism

MA[•] and OH free radicals (R[•]) are generated by the interaction of peroxymonosulphate ion and mandelic acid. They abstract hydrogen atom from chitosan and produce ChO[•] and ChNH[•] macroradical respectively at the OH and NH₂ sites of the chitosan molecule. The *N,N*-dimethylacrylamide (DMA) molecules which are in close vicinity of the reaction sites become acceptor of chitosan radical resulting in chain initiation of graft copolymer and thereafter themselves become free radical donor to neighbouring molecules. In this way grafted chain grows. These chains are terminated by coupling to give graft copolymer. The following tentative mechanism has been proposed.



Initiation:

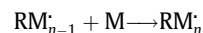
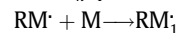
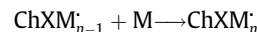
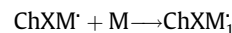


where X = O or NH

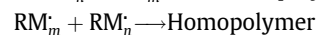
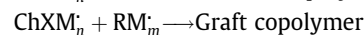
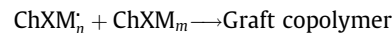
M = monomer



Propagation:



Termination:



3.4. Evidence of grafting

3.4.1. IR spectroscopy of chitosan and chitosan-g-*N,N*-dimethylacrylamide

Infra red spectrum of chitosan (Mishra, Tripathy, Mishra, Srivastava, & Behari, 2008a) showed strong peaks at 3388.3 and 1593.4 cm⁻¹ due to OH stretching and NH bending vibrations respectively. Band due to C–H deformation appeared at 885 cm⁻¹. The strong peaks at 1027, 1059, 1161 cm⁻¹ are due to O–H bending, C–O stretching and C–N stretching of chitosan. On comparing the IR spectra of chitosan and chitosan-g-DMA ((Fig. 2), it is observed that

Table 3

Effect of temperature. [DMA] = 22 × 10⁻² mol dm⁻³, [PMS] = 10 × 10⁻³ mol dm⁻³, [MA] = 3.2 × 10⁻³ mol dm⁻³, [ChXH] = 1.0 g dm⁻³, [H⁺] = 7 × 10⁻³ mol dm⁻³, time = 120 min.

Temp. (°C)	%G	%E	%A	%C	%H
25	68.6	72.0	40.7	6.2	28.0
30	125.6	75.2	55.7	9.2	24.8
35	192.5	81.4	65.8	10.8	18.6
40	205.0	83.6	67.2	11.2	16.4
45	128.0	74.9	43.9	9.4	25.1

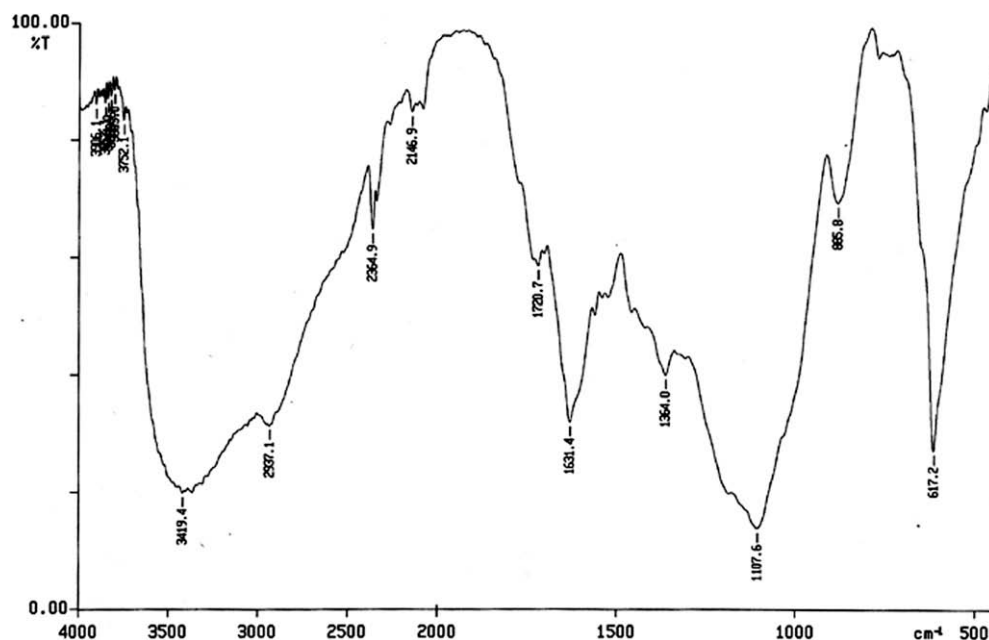


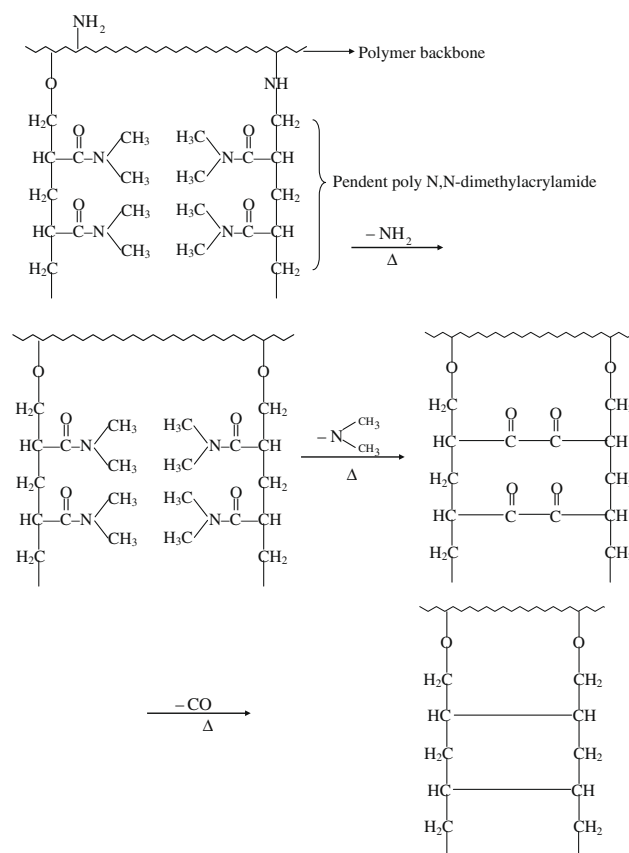
Fig. 2. IR spectrum of Chitosan-g-*N,N*-dimethylacrylamide.

there is variation in intensity of OH and N–H stretching vibration and shifting of peaks, which shows that there is appreciable grafting at these sites. The $-\text{CH}_2$ stretching band and intense peak of methylene C–H bending of grafted chains appeared at 2937.1 and 1364.0 cm^{-1} , respectively in the spectrum of graft copolymer. The grafting of monomer in the IR spectrum of grafted chitosan, is further confirmed by characteristics absorption bands at 1720.7 and 1364.0 cm^{-1} due to C=O stretching vibration C–N stretching vibration of tertiary amide. C–O–C stretching vibration at 1107.6 cm^{-1} confirms the attachment of monomer molecules to substrate through ether linkage at OH sites of substrate i.e. chitosan, in the spectrum of graft copolymer. N–H stretching is observed at 3419.4 cm^{-1} . The presence of additional bands, disappearance of in plane bending vibration of OH and shifting of N–H stretching from the spectrum of chitosan-g-DMA shows that grafting might have taken place at OH and NH_2 sites of backbone chitosan.

3.4.2. Thermal analysis of chitosan and chitosan-g-N,N-dimethylacrylamide

Thermogravimetric analysis curve of chitosan (Mishra, Tripathy, Mishra, Srivastava, & Behari, 2008b) shows single step degradation. The 16.3% weight loss at 93.8°C temperature might be due to loss of absorbed water. It starts to degrade at 114°C . The polymer decomposition temperature (PDT) has been found at 157°C . The rate of weight loss increases with increase in temperature from 186.3 to 218.3°C and thereafter decreases and attains a maximum value at about 512.5°C . T_{max} , temperature at which maximum degradation occurred, is 300°C (Fig. 3) which is also confirmed by a sharp endothermic peak present in DTA curve of chitosan at 310°C . The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at 700 and 248.4°C respectively.

The weight loss of 10% at 125°C is due to the loss of absorbed and bound water. The graft copolymer starts degrading at about 160°C and the rate of weight loss increased up to 190°C . The degradation appears to be a three-step process. The rate of weight loss increases with increase in temperature from 160°C and thereafter it slowly decreases up to 200°C then once again it degrades rapidly with weight loss of 33.125% up to 300°C and thereafter rate of weight loss decreases. In the third step the degradation starts from



Scheme 1. Schematic presentation of degradation pathway of graft copolymer.

710°C and attains a maximum value of 55% weight loss at 863°C . Thus three T_{max} have been observed in the degradation of chitosan-g-N,N-dimethylacrylamide i.e. at 188 , 250 and 813°C , respectively (Scheme 1). The polymer decomposition temperature (PDT) is found to be at 169°C . A weight loss of 50% occurs at 806°C . The final decomposition temperature (FDT) and integral procedural

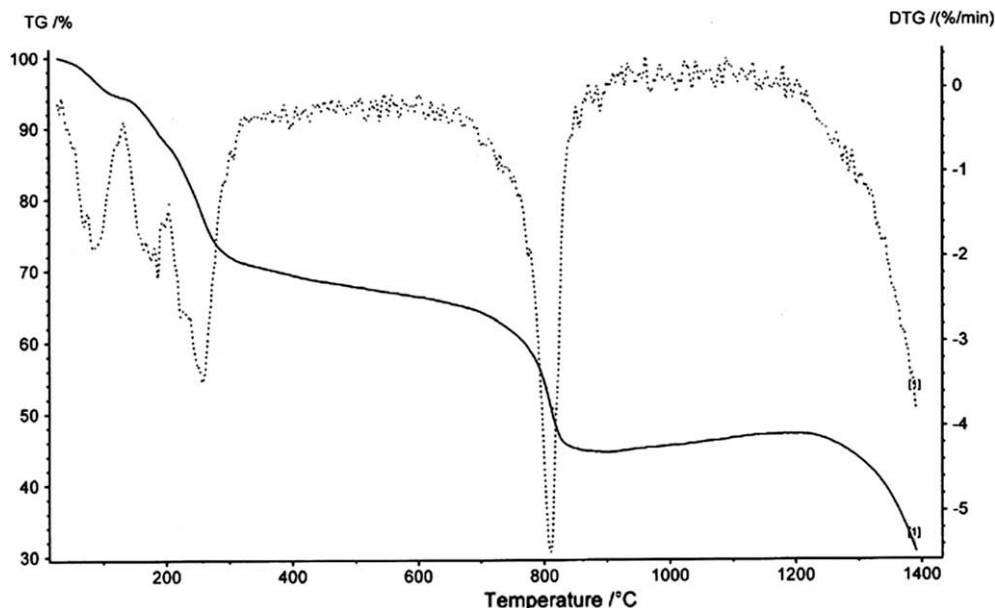


Fig. 3. Thermogravimetric trace of chitosan-g-N,N-dimethylacrylamide.

Table 4[ChXH] = 1.0 g dm⁻³, [PMS] = 10 × 10⁻³ mol dm⁻³, [MA] = 3.2 × 10⁻³ mol dm⁻³, [H⁺] = 7 × 10⁻³ mol dm⁻³, temp. = 35 °C, time = 120 min.

Sample	[DMA] × 10 ² mol dm ⁻³	%G	Percent uptake (P_u)					Partition coefficient (K_d)					Retention capacity (Q_r)				
			Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺
ChXH	–	–	4.6	3.2	4.2	3.3	0.6	24.2	16.3	22.2	17.3	3.2	2.2	1.6	2.0	1.7	0.3
A	14	136.2	6.5	4.4	6.1	4.5	1.9	34.8	23.8	35	24.2	9.7	3.1	2.3	3.0	2.4	0.9
B	18	168.0	8.4	5.9	8.4	6.0	3.1	45.8	31.5	45	32.2	16.4	4.0	3.0	3.9	3.1	1.5
C	22	192.4	10.1	7.1	9.2	7.9	4.4	55.9	38.5	50.7	42.7	23.3	4.8	3.6	4.4	3.8	2.1
D	26	220.3	12.4	8.1	10.1	9.3	5.7	70.5	44.1	56	51.0	30.4	5.9	4.1	4.8	4.2	2.7
E	30	254.3	13.8	9.5	11.1	10.0	7.2	80.3	52.4	62.5	55.5	38.9	6.6	4.8	5.4	5.0	3.4

where ChXH = chitosan; A, B, C, D and E are graft copolymers of chitosan and *N,N*-dimethylacrylamide.

decomposition temperature of grafted sample are found at 957 and 342.6 °C, respectively. High value of IPDT, FDT and 46% char yield at 900 °C of graft copolymer supports the thermal stability in comparison to ungrafted chitosan.

3.5. Properties

3.5.1. Swelling studies

The percent swelling and swelling ratio increase with increase in grafting, which is dependent upon monomer concentration. It has been observed that a maximum percent swelling of 570% occurs when grafting ratio is 254.3%. Since *N,N*-dimethylacrylamide is a hydrophilic monomer, it increases the water absorbing capacity and water retention character of graft copolymer. The increment in monomer concentration favours formation of longer pendant chain of poly (*N,N*-dimethylacrylamide) chain, which coils and traps water molecules and thus helps in holding more water molecules.

3.5.2. Metal ion sorption behaviour of chitosan and its graft copolymer

The results of sorption behaviour of chitosan and its grafted polymer with *N,N*-dimethyl acrylamide has been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r). The results are given in Table 4. 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 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 Hg²⁺ was least uptakable in comparison to four metal ions, which have been used.

3.5.3. 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 chitosan and graft copolymer of chitosan with *N,N*-dimethylacrylamide. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in (Fig. 4). It has been found that grafted copolymer (chitosan-*g-N,N*-dimethylacrylamide) shows better performance than chitosan 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 J., 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

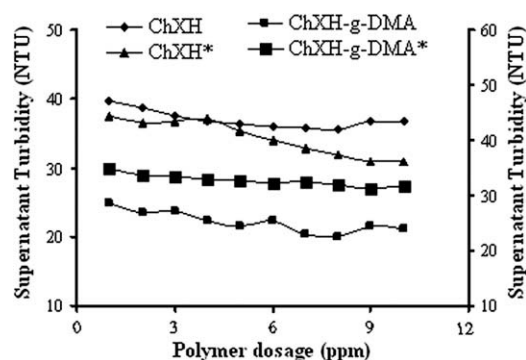


Fig. 4. Effect of polymer dosage on turbidity for coking and non-coking coal*.

of poly *N,N*-dimethylacrylamide onto chitosan, efficient flocculant has been obtained.

4. Conclusion

The spectroscopic data confirm that the grafting of *N,N*-dimethylacrylamide might have taken place at hydroxyl groups and amino groups, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that the grafted polymer is more thermally stable than pure chitosan. Our synthesized graft copolymer i.e. ChXH-*g-DMA* shows better results for swelling thus it could be interpreted that graft copolymer shows enhancement of the properties due to grafting, and thus could be exploited very well industrially.

Acknowledgement

Authors thankfully acknowledge to UGC, New Delhi for providing Emeritus fellowship to Kunj Behari.

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