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Graft copolymer (chitosan-g-*N*-vinyl formamide): Synthesis and study of its properties like swelling, metal ion uptake and flocculation

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ABSTRACT

A graft copolymer of chitosan and *N*-vinyl formamide has been synthesized by free radical polymerization using bromate/cyclohexanone redox in an inert atmosphere. The grafting ratio, add on, and efficiency increase continuously with increase in concentration of *N*-vinyl formamide from 9×10^{-2} mol dm^{-3} to 41×10^{-2} mol dm^{-3}, bromate ion from 0.4×10^{-2} mol dm^{-3} to 2.4×10^{-2} mol dm^{-3} and chitosan from 0.6 g dm^{-3} to 1.4 g dm^{-3}. Grafting parameters decrease with increase in concentration of hydrogen ion from 2×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3}. Experimental results also show that these parameters i.e. grafting ratio, add on, and efficiency increase with increase in cyclohexanone concentration from 0.4×10^{-2} mol dm^{-3} to 1.2×10^{-2} mol dm^{-3}, but beyond this cited range, these parameters decrease. Maximum grafting i.e. 189.5% has been found at 120 min and 40 °C. The swelling, metal ion sorption and flocculation capability have been studied, respectively. The flocculation capability of chitosan and chitosan-g-*N*-vinyl formamide in both coking and non-coking coals has been studied for the treatment of coal mine waste water. The graft copolymer has been characterized by Infra red (IR) spectroscopy and thermogravimetric analysis.

1. Introduction

Chitosan is currently at the focus of increasing scientific and economic interest among all polysaccharides owing to its significance in nature and technology. It is a basic polysaccharide in nature because of presence of amino group –NH_2 in its backbone. It is a polymer of β-(1,4) linked-2-amino-2-deoxy-D-glucopyranose derived by *N*-deacetylation of chitin in aqueous alkaline medium (Park, You, Park, Haam, & Kim, 2001). It occurs in marine invertebrates and shells of marine crustaceans i.e. shrimps and crabs (Hudson & Smith, 1998; Sashiwa, 2005). Due to its wide availability and unique chemical and biological properties such as biocompatibility, non-toxicity and antimicrobial properties (Denuziere, Ferrier, Damour, & Domard, 1998; Lee & Chen, 2001; Pourjavadia & Mahdavinia, 2006), it has found wide applications in a variety of areas such as biomedicine (Berger, Reist, Mayer, Felt, & Gurny, 2004; Jenkins & Hudson, 2002; Pourjavadi, Mahdavinia, Zohuriaan-Mehr, & Omidian, 2002; Yinghai, Zhenghao, Yanzhe, & Kuilin, 2002) and pharmaceutical industry (Jenkins & Hudson, 2001). In spite of its wide range applications, it suffers from drawback like biodegradability (Ravi Kumar, 2000), which limits its uses. This drawback can be improved by modification through grafting (Banerjee, Kumar, Srivastava, & Behari, 2006) of vinyl monomers onto it, thus graft copolymer will enhance the properties like swelling, metal ion uptake and flocculation.

N-vinyl formamide is a cationic hydrophilic monomer with relatively low toxicity (Macias, Kameneva, Tenhunen, Puyana, & Fink, 2004). With the availability of improved processes for synthesis and purification of *N*-vinyl formamide, Poly (*N*-vinyl formamide) and its derivatives are widely used in industry (Pinschmidt et al., 1997). Its various applications also include drainage aids as well as wet strength and dry strength agents for paper making (Linhart et al., 1988; Pfohl et al., 1988), in oil well drilling holes (Lai, Ta-Wang, Vijayendran, & Bheema, 1983). Poly (*N*-vinyl formamide) has also been found to be an effective drag reducing agent for biomedical applications (Marhefka, Marascalco, Chapman, Russell, & Kameneva, 2006). *N*-vinyl formamide has structural similarities with acrylamide, so graft copolymer of chitosan with it could be a good material for flocculation. Synthesized graft copolymers have resulted as better flocculant (Rath & Singh, 1997; Singh, 1995) with combined properties of both natural backbone as well as monomer.

In this article, a detail study of grafting has been made under a variety of different reaction conditions and the properties of graft copolymer (chitosan-g-*N*-vinyl formamide) such as swelling, metal ion sorption, along with flocculation have been presented to show better performance than their backbone chitosan. The synthesized graft copolymer of chitosan and *N*-vinyl formamide may be used as super absorbent, coating materials and flocculant to remove impurities from coal mine waste water.

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2. Experimental

2.1. Materials

N-vinyl formamide (Aldrich) was distilled under reduced pressure at 14 mm and 55 °C and only middle fraction was used. Cyclohexanone (E. Merck) was distilled at room temperature 35 °C and used as reductant. Chitosan purchased from (Sigma) USA and potassium bromate (E. Merck) were used as such. For maintaining hydrogen ion concentration sulphuric acid (E. Merck) has been used. The other reagents were of analytical grade. All the solutions were prepared in triple distilled water. For flocculation studies, coking and non-coking coals were used received from Steel Plant, Bokaro, India.

2.2. Procedure for Graft Copolymerization

All reactions were carried out under oxygen free nitrogen atmosphere. For each experiment chitosan solution has been prepared by adding desired amount of chitosan to a mixture of acetic acid and triple distilled water in a reactor kept in a thermostat at the desired temperature. A calculated amount of *N*-vinyl formamide (from 9×10^{-2} mol dm^{-3} to 41×10^{-2} mol dm^{-3}), cyclohexanone (from 0.4×10^{-2} mol dm^{-3} to 1.2×10^{-2} mol dm^{-3}) and sulphuric acid (from 2×10^{-3} mol dm^{-3} to 10×10^{-3} mol dm^{-3}) solutions have been added to the reactor containing chitosan (0.6–1.4 g dm^{-3}) solutions. A known amount of bromate (from 0.4×10^{-2} mol dm^{-3} to 2.4×10^{-2} mol dm^{-3}) solutions has been added to initiate the reaction, which is deoxygenated by passing nitrogen gas for half an hour. After a desired interval of time, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring the reaction mixture into water–methanol mixture. The precipitate has been filtered and dried and weighed. The filtrate has been concentrated by distillation under the reduced pressure in the presence of little amount of hydroquinone. The poly *N*-vinyl formamide was precipitated by pouring the concentrated filtrate into pure methanol. Poly *N*-vinyl formamide thus obtained, has been separated, dried and weighed.

2.3. Estimation of grafting parameters

The graft copolymer has been characterized according to (Fanta, 1973) Fanta definition.

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

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

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

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

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

The effect of variation of cyclohexanone, bromate ion, sulphuric acid, *N*-vinyl formamide, chitosan concentration along with time and temperature on grafting parameters has been studied.

2.4. Method of characterization of chitosan/chitosan-g-N-vinyl formamide

2.4.1. IR spectroscopy

The IR spectra of chitosan and grafted samples have been recorded with JASCO FT/IR-5300 model in the range 500–4000 cm^{-1} to provide the proof of the grafting.

2.4.2. Thermogravimetric 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 an atmosphere of nitrogen.

2.5. Study of properties

2.5.1. Swelling

The swelling capacity of different samples of graft copolymer has been studied. The different samples of graft copolymer have been synthesized at different concentrations of monomer. The pre weighed 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 triple distilled water, quickly wiped with filter paper to remove droplets on the surface and weighed. The percent swelling (P_s) and swelling ratio (S_r) have been calculated by using following expressions (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000).

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

$$S_r = \frac{\text{Weight of swollen polymer} - \text{Weight of dry polymer}}{\text{Weight of dry polymer}}$$

2.5.2. Metal ion uptake

The metal ion sorption studies have been carried out on graft copolymer of different compositions, which have been synthesized by varying the concentration of *N*-vinyl formamide from 9×10^{-2} mol dm^{-3} to 41×10^{-2} mol dm^{-3}. For this 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 unabsorbed metals solution has been determined by standard method. For metal ion sorption studies we have chosen five metal ions i.e. Cu^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+} and Hg^{2+}. Sorption behaviour of polymeric backbone and graft copolymer for five metals ions have been investigated by using following parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998).

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

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

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

2.5.3. Flocculation

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

3. Results and discussion

3.1. Mechanism

It is assumed that in the presence of sulphuric acid, during the oxidation of cyclohexanone by bromate ion, the free radicals like $\cdot C_6H_4O$, $\cdot CH$ and $Br^{\cdot}$ are produced. These all types of radicals, denoted by $\cdot R$, abstract hydrogen atom from chitosan molecule producing chitosan macro radical. The monomer molecules, which are in close vicinity of reaction sites, become acceptor of chitosan macro radicals, resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules leading to the propagation. These grafted chains are terminated by coupling to give graft copolymer On the basis of experimental results, a tentative mechanism can be represented as

$$C_6H_5O + BrO_3^- \rightarrow \cdot C_6H_4O + BrO_2^- + \cdot OH$$
$$C_6H_5O + BrO_2^- \rightarrow \cdot C_6H_4O + BrO^- + \cdot OH$$
$$C_6H_5O + BrO^- \rightarrow \cdot C_6H_4O + Br^{\cdot} + OH^-$$

where $\cdot R = \cdot C_6H_4O, OH^{\cdot}$ and $Br^{\cdot}$.

3.1.1. Initiation

$$M + R^{\cdot} \rightarrow RM^{\cdot}$$
$$\underset{\text{chitosan}}{ChXH} + R^{\cdot} \rightarrow \underset{\text{macro radicals}}{ChX^{\cdot}} + RH$$

where X = O or NH, M = monomer, $ChX^{\cdot} = ChO^{\cdot}$ or $ChNH^{\cdot}$ (macro radical).

3.1.2. Propagation

$$ChX^{\cdot} + M \rightarrow ChXM^{\cdot}$$
$$ChXM^{\cdot} + M \rightarrow ChXM_1^{\cdot}$$
$$ChXM_1^{\cdot} + M \rightarrow ChXM_2^{\cdot}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$ChXM_{n-1}^{\cdot} + M \rightarrow ChXM_n^{\cdot}$$
$$RM^{\cdot} + M \rightarrow RM_1^{\cdot}$$
$$RM_1^{\cdot} + M \rightarrow RM_2^{\cdot}$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$
$$RM_{n-1}^{\cdot} + M \rightarrow RM_n^{\cdot}$$

3.1.3. Termination

$$ChXM_n^{\cdot} + ChXM_m^{\cdot} \rightarrow \text{Graft copolymer}$$
$$ChXM_n^{\cdot} + RM_n^{\cdot} \rightarrow \text{Graft copolymer}$$
$$RM_n^{\cdot} + RM_m^{\cdot} \rightarrow \text{Homopolymer}$$

3.2. Effect of N-vinyl formamide

The effect of concentration of *N*-vinyl formamide on grafting parameters has been studied by varying the concentration *N*-vinyl formamide from 9×10^{-2} mol dm^{-3} to 41×10^{-2} mol dm^{-3}. The results are shown in Fig. 1. It has been observed that grafting ratio, add on, and efficiency increase whereas homopolymer decreases continuously with increase in monomer concentration. The increment in grafting parameters could be explained by the fact that the greater availability of monomer molecules was at the close proximity of polymer backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of chitosan macro radicals ($ChX^{\cdot}$) resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring monomer molecules causing the lowering the termination.

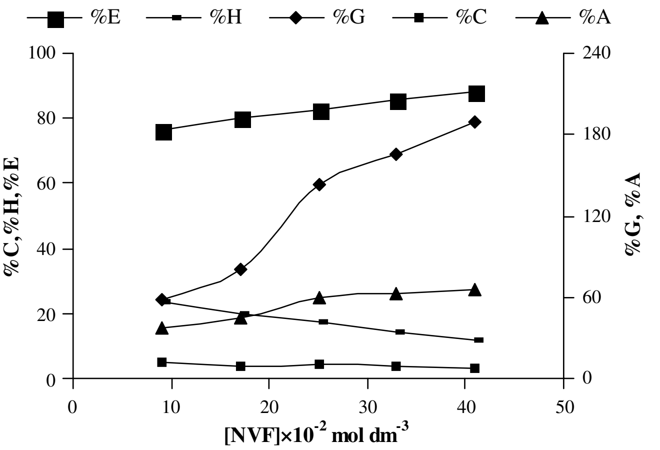

Fig. 1. Effect of NVF. [ChXH] = 1.0 g dm^{-3}; [BrO$_3^-$] = 1.4×10^{-2} mol dm^{-3}; time = 120 min; [CY] = 12×10^{-3} mol dm^{-3}; [H$^+$] = 6×10^{-3} mol dm^{-3}; temperature = 40 °C.

3.3. Effect of cyclohexanone

The effect of concentration of cyclohexanone on grafting parameters has been studied by varying the concentration of cyclohexanone from 0.4×10^{-3} mol dm^{-3} to 2.0×10^{-3} mol dm^{-3}. The results are given in Table 1. It is clear that grafting ratio, add on, conversion and efficiency increase on increasing the concentration of cyclohexanone from 0.4×10^{-3} mol dm^{-3} to 1.2×10^{-3} mol dm^{-3}, but beyond cited range, these parameters decrease and homopolymer increases with increase in concentration of cyclohexanone. The increment in grafting ratio, add on, and efficiency might be due to increase in number of primary free radicals but at higher concentration from 1.2×10^{-3} mol dm^{-3} to 2.0×10^{-3} mol dm^{-3}grafting ratio, add on, and efficiency decrease because higher concentration favours the formation of poly (NVF) over grafting.

3.4. Effect of BrO_3^- ion

The effect of bromate concentration on graft copolymerization has been studied at different concentration of bromate ion, and results are presented in Fig. 2. It has been found that grafting ratio, add on, efficiency and conversion increase on increasing the concentration of bromate ion whereas homopolymer decreases. The continuous increment in grafting parameters might be due to progressive reduction of bromate ion by cyclohexanone producing more primary free radicals (Behari, Chatterjee, & Pandey, 1981), which attack on chitosan molecule creating more active sites to which monomer addition takes place.

Table 1
Effect of cyclohexanone

[CY] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
0.4	26.9	71.9	21.2	2.1	28.1
0.8	66.6	76.4	39.9	4.9	23.6
1.2	143.5	82.8	58.9	9.8	17.2
1.6	110.2	77.2	52.4	8.0	22.8
2.0	69.72	76.3	41.1	5.1	23.7

[ChXH] = 1.0 g dm^{-3}, [BrO$_3^-$] = 1.4×10^{-2} mol dm^{-3}, [NVF] = 25×10^{-2} mol dm^{-3}, [H$^+$] = 6×10^{-3} mol dm^{-3}, temperature = 40 °C, time = 120 min.

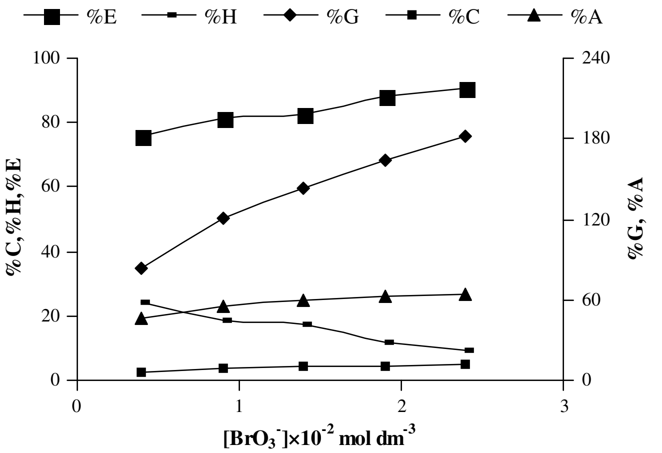

Fig. 2. Effect of BrO_3^-. [ChXH] = 1.0 g dm^{-3}; [BrO_3^-] = 1.4 × 10^{-2} mol dm^{-3}; time = 120 min; [CY] = 12 × 10^{-3} mol dm^{-3}; [NVF] = 25 × 10^{-2} mol dm^{-3}; temperature = 40 °C.

3.5. Effect of hydrogen ion

The effect of hydrogen ion concentration on grafting parameters has been studied by varying the concentration of sulphuric acid from 2 × 10^{-3} mol dm^{-3} to 10 × 10^{-3} mol dm^{-3}. The results are given in Table 2. The grafting ratio, add on, conversion and efficiency decrease but homopolymer increases continuously with increase in hydrogen ion concentration which is due to the fact that in the presence of excess hydrogen ion the bromate forms $HBrO_3$ species. This species further decomposes to give oxygen that acts as scavenger for free radicals so grafting parameters show decreasing trend.

$$KBrO_3 + H^+ \rightarrow HBrO_3$$
$$4HBrO_3 \rightarrow 2Br_2 + 2H_2O + 5O_2 \uparrow$$

3.6. Effect of temperature

The effect of temperature on grafting parameters has been studied at various temperatures. The results are shown in Fig. 3. It has been found, as the temperature is increased from 30 °C to 40 °C, grafting ratio, add on, conversion and efficiency increase. But beyond 40 °C, these parameters decrease. The increase in grafting ratio, add on and efficiency with temperature from 30 °C to 40 °C might be due to the rate of production of primary free radicals increases which generates grafting sites at greater rate, thereby, increasing the value of these parameters. However, beyond 40 °C grafting parameters decreased and homopolymer increased. The decrement in grafting parameters is attributed to the premature termination of growing grafted chain at higher temperature.

3.7. Effect of time

The effect of change in duration on grafting parameters has been studied by varying the time period from 60 min to 180 min The results are summarized in Table 3. It is clear from table that grafting ratio, add on, conversion and efficiency increase with increase in time period from 60 min to 120 min but homopolymer decreases and thereafter these parameters decrease and homopolymer increases. On increasing the time period propagation of grafting chains takes place at faster rate due to availability of more active sites, which account for higher grafting. On further increasing time interval, the mutual annihilation of growing grafted chains might occur so grafting parameters decrease.

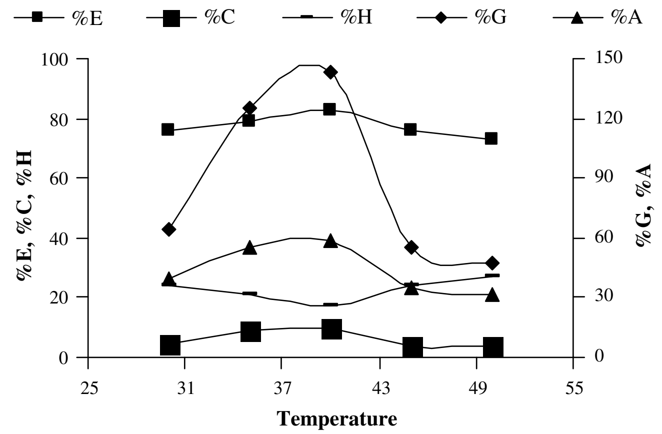

Fig. 3. Effect of temperature. [ChXH] = 1.0 g dm^{-3}; [BrO_3^-] = 1.4 × 10^{-2} mol dm^{-3}; time = 120 min; [NVF] = 25 × 10^{-2} mol dm^{-3}; [CY] = 12 × 10^{-3} mol dm^{-3}; [H$^+$] = 6 × 10^{-3} mol dm^{-3}.

3.8. Effect of chitosan

The effect of concentration of chitosan on grafting parameters has been studied by varying the concentration of chitosan from 0.6 g dm^{-3} to 1.4 g dm^{-3}. The results are shown in Fig. 4. It has been found that grafting ratio, add on, conversion and efficiency increase with increase in concentration of chitosan, might be attributed to the fact that the availability of more and more grafting sites at chitosan resulting in increment in grafting parameters and decrement in homopolymer.

3.9. Evidence of grafting

Infra red spectrum of chitosan showed two strong peaks at 3388.3 cm^{-1} and at 1593.4 cm^{-1} due to OH stretching vibration and NH bending vibration, respectively. On comparing the IR spectra of chitosan and chitosan-*N*-vinyl formamide, Chitosan-g-*N*-vinyl formamide showed variations in intensity of OH stretching and NH bending vibrations. The shifting of peak from 3388.3 cm^{-1} to 3120.1 cm^{-1} appeared due to OH stretching vibration and disappearance of peak appeared at 1593.4 cm^{-1} due to NH bending vibration from the spectrum of chitosan indicating the participation of hydroxyl and amino groups in chemical reaction. The grafting of monomer is further confirmed by characteristic

Table 2
Effect of hydrogen ion

[H$^+$] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
2	182.2	90.6	64.6	11.3	9.4
4	164.3	87.9	62.2	10.5	12.1
6	143.5	82.8	58.9	9.8	17.2
8	122.4	78.3	55.0	7.1	21.7
10	110.2	77.2	52.4	8.0	22.8

[ChXH] = 1.0 g dm^{-3}, [BrO_3^-] = 1.4 × 10^{-2} mol dm^{-3}, [CY] = 12 × 10^{-3} mol dm^{-3}, [NVF] = 25 × 10^{-2} mol dm^{-3}, temperature = 40 °C, time = 120 min.

Table 3
Effect of time

Time (min)	%G	%E	%A	%C	%H
60	95.8	70.7	48.9	7.6	29.3
90	123.9	74.9	55.3	9.3	25.1
120	143.5	82.8	58.9	9.8	17.2
150	65.8	78.8	39.7	4.7	21.3
180	61.3	74.1	37.9	4.7	25.9

[ChXH] = 1.0 g dm^{-3}, [BrO_3^-] = 1.4 × 10^{-2} mol dm^{-3}, [CY] = 12 × 10^{-3} mol dm^{-3}, [NVF] = 25 × 10^{-2} mol dm^{-3}, [H$^+$] = 6 × 10^{-3} mol dm^{-3}, temperature = 40 °C.

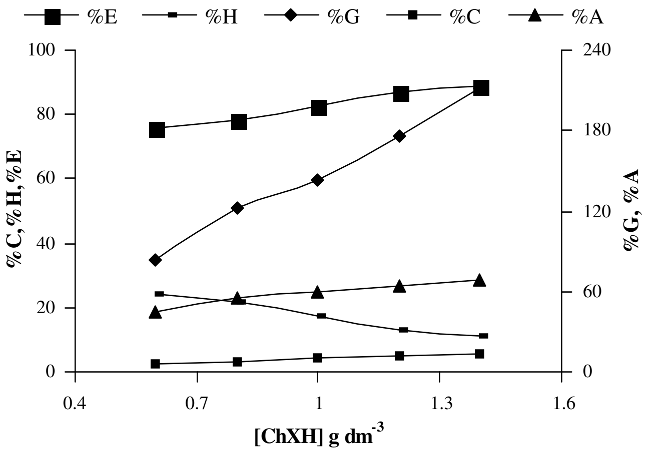

Fig. 4. Effect of chitosan. [NVF] = 25 × 10^{-2} mol dm^{-3}; [BrO_3^-] = 1.4 × 10^{-2} mol dm^{-3}; time = 120 min; [CY] = 12 × 10^{-3} mol dm^{-3}; temperature = 40 °C.

absorption band at 3501.3 cm^{-1} due to appearance N–H stretching vibration (Amide II) of pendant chain of monomer molecule results from the interaction between N–H bending vibration and CN stretching vibration, respectively, (presented graph in Fig. 5). A band at 1121.3 cm^{-1} is due C–N stretching vibration of secondary amide present in pendant chain of monomer. The appearance of additional peaks due to the pendant chain of monomer in graft copolymer as well as disappearance of OH bending and NH bending vibrations from the spectrum of chitosan-*N*-vinyl formamide which appeared at 669.0 cm^{-1} and 1513.4 cm^{-1}in chitosan, respectively, suggest that grafting might have taken place on OH and NH_2 sites of backbone.

3.10. Thermogravimetric analysis

Thermogravimetric analysis curve of chitosan shows single step degradation. The 16.3% weight loss at 93.8 °C might be due to loss of absorbed water. It starts to degrade at 114.0 °C. The polymer decomposition temperature (PDT) has been found at 157.0 °C. The rate of weight loss increases with increase in temperature from 186.3 °C 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 300.0 °C which is also confirmed by a sharp endothermic peak present in DTA curve of chitosan at 310.0 °C. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at 700.0 °C and 248.4 °C, respectively. But in case of chitosan-g-*N*-vinyl formamide, it has been found that degradation of chitosan-g-*N*-vinyl formamide starts to degrade at about 106.3 °C temperature (presented in Fig. 6). The polymer decomposition temperature (PDT) has been found at 113 °C. The weight loss at about 118.8 °C might be due to absorbed water. The rate of weight loss increases with increase in temperature from 150.0 °C to 300.0 °C and thereafter decrease and attains a maximum value at about 800.0 °C, therefore final decomposition temperature (FDT) has been found high i.e. 968.0 °C. The degradation of graft copolymer has been taken place in two steps i.e. between 150.0 °C to 218.0 °C and 250.0 °C to 300.0 °C temperature ranges. Two $T_{max,}$ temperatures at which maximum degradation occurs, have been found at 262.5 °C and 306.3 °C, respectively. First $T_{max,}$ at 262.5 °C might due to loss of –CO group from pendant chain attached to the polymeric backbone, which is also confirmed by endothermic peak present in DTA curve (Fig. 7) of chitosan-g-*N*-vinyl formamide at 275.7 °C. The second T_{max} might be due to the elimination of functional –NH_2 group from pendant chain attached to chitosan backbone, which is confirmed by endothermic peak present in DTA curve of graft copolymer at 306.9 °C. The final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) have been found at 968.0 °C and 199.7 °C, respectively. The two steps degradation and high values of final decomposition temperature favour the thermal stability of graft copolymer in comparison to the backbone.

3.11. Swelling

It has been observed from the results (given in Table 4) that percent swelling and swelling ratio of graft copolymer increase with increase in the percent grafting that depends on monomer concentration. The percentage of hydrophilic character in graft copolymer increases with increasing chain of pendent poly (*N*-vinyl formamide) onto chitosan thereby increasing swelling capability of graft copolymer.

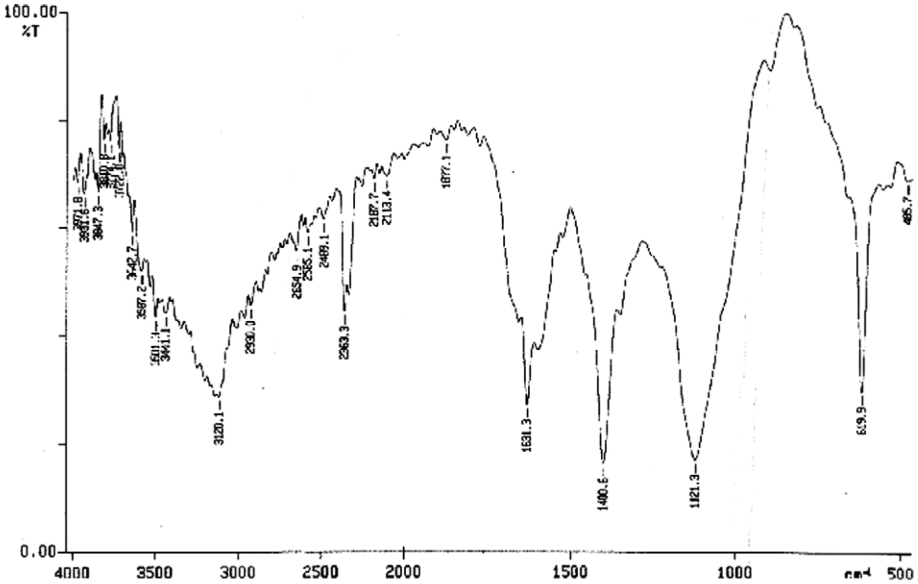

Fig. 5. IR spectrum of chitosan-*N*-vinyl formamide.

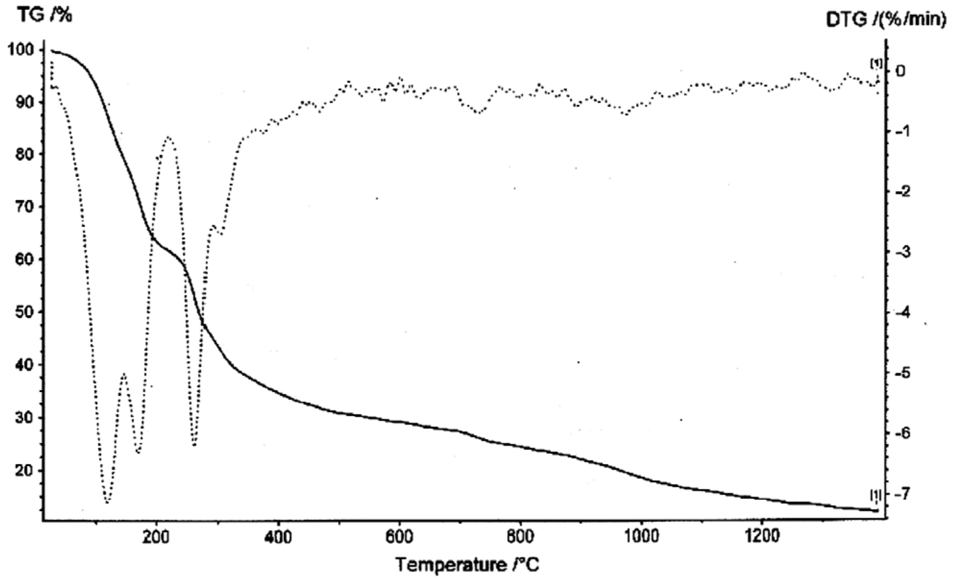

Fig. 6. Thermogravimetric trace of chitosan-*N*-vinyl formamide.

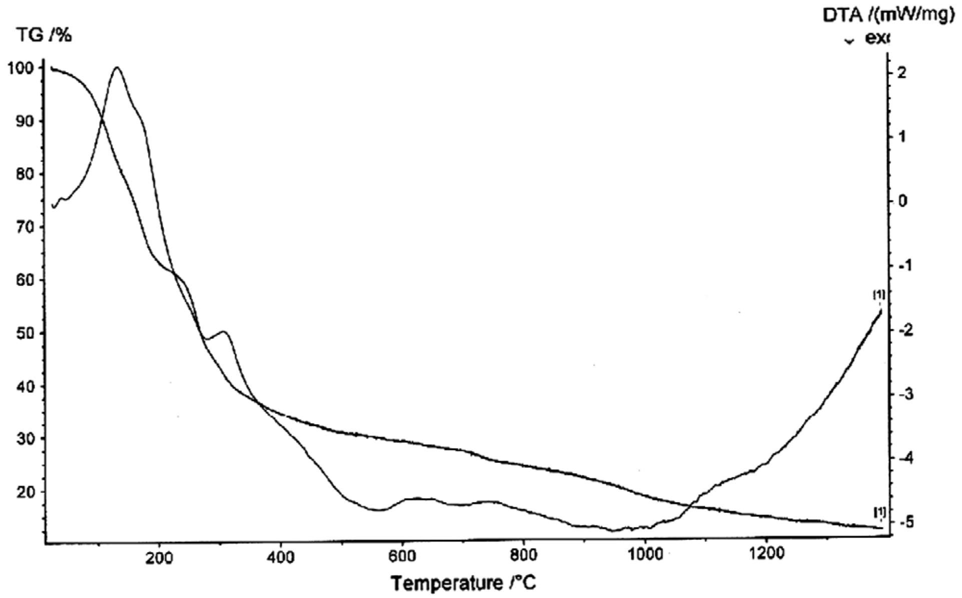

Fig. 7. Differential thermal trace of chitosan-*N*-vinyl formamide.

3.12. Metal ion sorption

The results of sorption behaviour of chitosan and its grafted polymer with *N*-vinyl formamide have been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r). It has been observed that the value of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly as percent grafting increases (results given in Table 5), which might be due to the increase in pendent chain of poly (*N*-vinyl formamide). Results also show that Hg^{2+} was least uptakable in comparison to four metal ions of them, which have been used.

Table 4
Swelling capacity of chitosan-g-*N*-vinyl formamide

Sample code	[NVF] × 10^2 mol dm^{-3}	%G	P_s	S_r
C_{N1}	9	58.1	113	1.1
C_{N2}	17	80.5	198	1.9
C_{N3}	25	143.5	276	2.8
C_{N4}	33	165.4	342	3.4
C_{N5}	41	189.4	410	4.1

[ChXH] = 1.0 g dm^{-3}, [CY] = 12 × 10^{-3} mol dm^{-3}, $[BrO_3^-] = 1.4 \times 10^{-2}$ mol dm^{-3}, [H$^+$] = 6 × 10^{-3} mol dm^{-3}, time = 120 min, temperature = 40 °C.

3.13. Flocculation

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquid have been taken as the measurement of flocculation efficiency of backbone chitosan and graft copolymer of *N*-vinyl formamide with chitosan. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are presented in Figs. 8 and 9. It is obvious that grafted copolymer

Table 5
Sorption studies of metal ions on chitosan and chitosan-g-*N*-vinyl formamide

Sample code	[NVF] × 10^2 mol dm^{-3}	%G	Percent uptake (P_u)					Partition coefficient (K_d)					Retention capacity (Q_r)				
			Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Hg^{2+}
C	–	–	2.9	2.1	1.1	2.2	1.2	14.9	10.5	5.8	11.2	6.2	1.4	1.0	0.6	1.1	0.6
C_{N1}	9	58.1	3.7	2.9	2.1	2.6	1.6	19.4	14.8	10.7	13.2	8.3	1.8	1.4	1.1	1.3	0.8
C_{N2}	17	80.5	5.4	4.3	3.4	3.9	2.2	28.5	22.6	17.7	20.7	11.5	2.6	2.1	1.8	2.0	1.1
C_{N3}	25	143.5	8.3	7.8	5.3	7.1	4.3	45.2	42.4	28.1	38.5	22.4	4.0	3.8	2.8	3.6	2.1
C_{N4}	33	165.4	11.4	10.5	9.5	9.9	6.7	64.4	58.6	52.5	55.1	36.2	5.5	5.1	5.0	5.0	3.3
C_{N5}	41	189.4	13.9	11.9	10.6	11.3	8.6	80.7	67.8	59.6	63.8	46.9	6.7	5.8	5.6	5.7	4.2

Where C, chitosan, C_N, chitosan-g-*N*-vinyl formamide.
[ChXH] = 1.0 g dm^{-3}, [NVF] = 25 × 10^{-2}, [BrO_3^-] = 1.4 × 10^{-2} mol dm^{-3}, [CY] = 12 × 10^{-3} mol dm^{-3}, [H^+] = 6.0 × 10^{-3} mol dm^{-3}, time = 120 min, temperature = 40 °C.

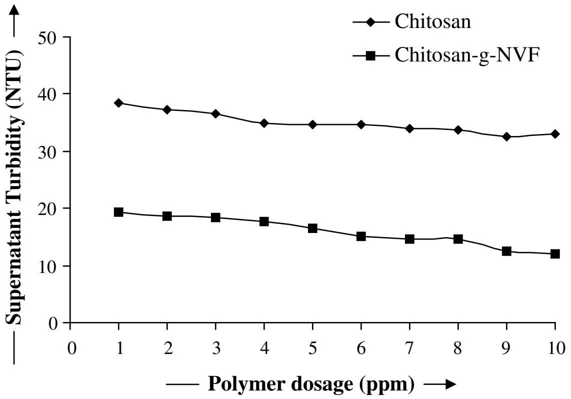

Fig. 8. Effect of polymer dosage on turbidity for coking coal.

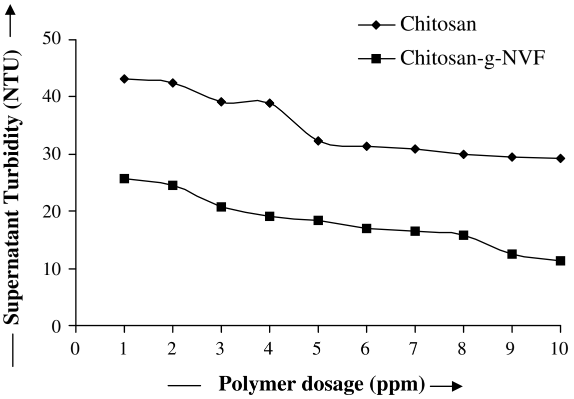

Fig. 9. Effect of polymer dosage on turbidity for non-coking coal.

(chitosan-g-*N*-vinyl formamide) shows better performance with low turbidity than chitosan itself. This phenomenon could be explained by considering bridging mechanism (Gregory, 1982). In grafted copolymer, the dangling of poly (*N*-vinyl formamide) chains has better approachability (Deshmukh, Chaturvedi, & Singh, 1985) to the contaminant coal particles hence increasing its flocculation capability. By grafting of poly *N*-vinyl formamide onto chitosan, efficient flocculant has been obtained and it may be used for the treatment of coal mine waste water.

4. Conclusions

The thermal data show that the synthesized graft copolymer is thermally more stable than pure chitosan. The synthesized graft copolymer i.e. chitosan-g-*N*-vinyl formamide shows better results for swelling, metal ion sorption and flocculating properties in comparison to chitosan, thus could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of *N*-vinyl formamide might have taken place at hydroxyl and amino groups, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft copolymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well industrially.

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References

Abd EL-Rehim, H. A., Hegazy EL-Sayed, A., & Ali, A. M. (2000). Selective separation of some heavy metals by poly (vinyl alcohol)-grafted membranes. *Journal Applied Polymer Science, 76*(2), 125–132.

Banerjee, J., Kumar, R., Srivastava, A., & Behari, K. (2006). Graft copolymerization of 2-acrylamido-2-methyl-1-propanesulphonic acid onto carboxymethylcellulose (sodium salt) using bromate/thiourea redox pair. *Journal of Applied Polymer Science, 100*, 26.

Behari, K., Chatterjee, H., & Pandey, N. N. (1981). Cyclohexanone and 2-methyl cyclohexanone by cerium sulphate in aqueous sulphuric acid medium. *Zeitschrift fur Physikalische Chemie (Leipzig), 262*(2), S. 273 .

Berger, J., Reist, M., Mayer, J. M., Felt, O., & Gurny, R. (2004). Structure and interactions in chitosan hydrogels formed by complexation or aggregation for biomedical applications. *European Journal of Pharmaceutics and Biopharmaceutics, 57*, 35.

Denuziere, A., Ferrier, D., Damour, O., & Domard, A. (1998). Chitosan–chondroitin sulfate and chitosan–hyaluronate polyelectrolyte complexes: Biological properties. *Biomaterials, 19*, 1275.

Deshmukh, S. R., Chaturvedi, P. N., & Singh, P. N. (1985). The turbulent drag reduction by graft copolymers of guar gum and polyacrylamide. *Journal Applied Polymer Science, 30*, 4013.

Fanta, G. F. (1973). Properties and applications of graft and block copolymers of starch. In R. J. Ceresa (Ed.), *Block and graft copolymerization* (pp. 29–45). New York, NY, London, England: Wiley-Interscience.

Gregory, J. (1982). Polymer flocculation in flowing dispersions. In T. F. Tadros (Ed.), *The effect of polymers on dispersion properties*. London: Academic Press.

Hudson, S. M., & Smith, C. (1998). Polysaccharides: Chitin & Chitosan chemistry and technology of their use as structural materials. In D. L. Kaplan (Ed.), *Biopolymers from renewable resources* (pp. 115). Berlin, Heidelberg, Newyork: Springer-Verlag.

Jenkins, D. W., & Hudson, S. M. (2001). Review of vinyl graft copolymerization featuring recent advances toward controlled radical-based reactions and illustrated with chitin/chitosan trunk polymers. *Chemical Reviews, 101*, 3245.

Jenkins, D. W., & Hudson, S. M. (2002). Heterogeneous graft copolymerization of chitosan powder with methyl acrylate using trichloroacetyl-manganese carbonyl co-initiation. *Macromolecules, 35*, 3413.

Lai, Ta-Wang, Vijayendran, & Bheema, R. (1983), Cement composition for oil well drilling holes containing high molecular weight poly (vinylamines) U. S. Patent 4795770.

Lee, W. F., & Chen, Y. J. (2001). Studies on preparation and swelling properties of the *N*-isopropylacrylamide/chitosan semi-IPN and IPN hydrogels. *Journal of Applied Polymer Science, 82*, 2487.

Linhart, F., Degen, H., Auhorn, W., Kroener, M., Hartmann, H., & Heide, W. (1998), Production of paper, board and cardboard, U.S. Patent 4772359.

Macias, C. A., Kameneva, M. V., Tenhunen, J. J., Puyana, J. C., & Fink, M. P. (2004). Survival in a rat model of lethal hemorrhagic shock is prolonged following resuscitation with a small volume of a solution containing a drug-reducing polymer derived from aloe vera. *Shock, 22*, 151.

Marhefka, J. N., Marascalco, P. J., Chapman, T. M., Russell, A. J., & Kameneva, M. V. (2006). Poly (*N*-vinylformamide)-A drag-reducing polymer for biomedical applications. *Biomacromolecules, 7*, 1597.

Park, S. B., You, J. O., Park, H. Y., Haam, S. J., & Kim, W. S. (2001). A novel pH-sensitive membrane from chitosan TEOS IPN: Preparation and its drug permeation characteristics. *Biomaterials, 22*, 323.

Pfohl, Sigberg, Kroener, Michael, Hartman, Heinrich, Denzinger, & Walter. (1988). Preparation of water-soluble copolymers containing vinylamine units, and their use as wet strength agents and dry strength agents for paper U.S. Patent 4774285.

Pinschmidt, R. K., Jr., Renz, W. L., Carroll, W. E., Yacoub, Khalil, Drescher, Jennifer, Nordquist, A. F., et al. (1997). *N*-vinylformamide – Building block for novel polymer structures. *Journal of Macromolecular Science, Pure and Applied Chemistry, A34*, 1885.

Pourjavadia, A., & Mahdavinia, G. R. (2006). Superabsorbency P^H-sensitivity and swelling kinetics of partially hydrolyzed chitosan-g-poly (acrylamide) hydrogels. *Turkish Journal of Chemistry, 30*, 595.

Pourjavadi, A., Mahdavinia, G. R., Zohuriaan-Mehr, M. J., & Omidian, H. (2002). Modified chitosan. I. Optimized cerium ammonium nitrate-induced synthesis of chitosan-graft-polyacrylonitrile. *Journal of Applied Polymer Science, 88*, 2048.

Rath, S. K., & Singh, R. P. (1997). Flocculation characteristics of grafted and ungrafted starch, amylose and amylopectine. *Journal Applied Polymer Science*, 1721–1729.

Ravi Kumar, M. N. V. (2000). A review of chitin and chitosan applications. *Reactive and Functional polymers, 46*, 1–27.

Rivas, B. L., Maturana, H. A., Molina, M. J., Gomez-Anton, M. R., & Pierola, I. F. (1998). Metal ion binding properties of poly (*N*-vinylimidazole) hydrogels. *Journal Applied Polymer Science, 67*, 1109.

Sashiwa, S. (2005). Current aspects on chemical modification of chitosan. *Asian Journal, 1*, 1–12.

Singh, R. P. (1995). Advanced turbulent drag reducing and flocculating materials based on polysaccharides. In P. N. Prasad, J. E. Mark, & T. J. Fai (Eds.), *Polymer and other advanced materials: Emerging technologies and business opportunities* (pp. 227). New York: Plenum Press.

Yinghai, L., Zhenghao, L., Yanzhe, Z., & Kuilin, D. (2002). Graft copolymerization of methyl acrylate onto chitosan initiated by potassium diperiodatonickelate (IV). *Journal of Macromolecular Science, Pure Applied Chemistry, A39*(1–2), 129.