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Graft copolymerization of *N*-vinylformamide onto sodium carboxymethylcellulose and study of its swelling, metal ion sorption and flocculation behaviour

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ABSTRACT

The present paper reports the graft copolymerization of *N*-vinylformamide onto sodium carboxymethylcellulose by free radical polymerization using potassium peroxymonosulphate/thiourea redox system in an inert atmosphere. The reaction conditions for maximum grafting have been optimized by varying the reaction variables, including the concentration of *N*-vinylformamide (12.0×10^{-2}–28.0×10^{-2} mol dm^{-3}), potassium peroxymonosulphate (4.0×10^{-3}–12.0×10^{-3} mol dm^{-3}), thiourea (1.2×10^{-3}–4.4×10^{-3} mol dm^{-3}), sulphuric acid (2.0×10^{-3}–10.0×10^{-3} mol dm^{-3}), sodium carboxymethylcellulose (0.2–1.8 g dm^{-3}) along with time duration (60–180 min) and temperature (25–45° C). Water swelling capacity, metal ion sorption and flocculation studies of synthesized graft copolymer have been performed with respect to the parent polymer. The graft copolymer has been characterized by FTIR spectroscopy and thermogravimetric analysis.

1. Introduction

In recent years, there has been phenomenal growth in the field of functional materials based on graft copolymers (Fakhru'L-Razi, Qudsieh Isam, Yunus Wan Md Zin Wan, Ahmad Mansor, & Rahman Mohamad Zaki Ab, 2001; Patel, Patel, & Trivedi, 1999; Pourjavadi, Hosseinzadeh, & Mazidi, 2005). In the same way, in order to increase its paramount contribution towards their improved industrial applications (Chen & Wang, 2001; Yang & Yuan, 2001), the present study has been made which is concerned with the synthesis of a new type of graft copolymer of sodium carboxymethylcellulose and *N*-vinylformamide and some of the properties that have been investigated to make it more applicable. Various graft copolymers have been synthesized by graft copolymerization of vinyl monomers onto natural polymers in our laboratory (Banerjee, Srivastava, Srivastava, & Behari, 2006; Pandey, Srivastava, Tripathy, & Behari, 2006). Therefore sodium carboxymethylcellulose has been chosen a new type of polymeric backbone, which is water soluble cellulose ether, manufactured by reacting sodium monochloroacetate with cellulose in alkaline medium (Hader & Waldeck, 1952). Few research reports are available concerning with the use of sodium carboxymethylcellulose in controlled drug release (Lapidus & Lordi, 1968; Mitchell et al., 1990), in medicine as a tablet binder and to stabilize emulsions (Oza, & Frank, 1986; Sebert, Bourny, & Rollet, 1994). It has been found to have multifunctional characteristics as an oil field drilling (Zhang, Tan, & Li, 2000), viscosity building and filtration control (Tan, Zhang, & Li, 1998). Although sodium carboxymethyl cellulose has wide range of uses, but it suffers from a drawback i.e. biodegradability which limits its uses considerably. *N*-vinylformamide is a cationic hydrophilic monomer. With the availability of improved processes for synthesis and purification of *N*-vinylformamide, Poly (*N*-vinylformamide) and its derivatives are widely used industrially (Pinschmidt et al., 1997). Poly (*N*-vinylformamide) has also been found to be an effective drag reducing agent (Marhefka, Marascalco, Chapman, Russell, & Kameneva, 2006). Prompted by the applications of *N*-vinylformamide, hitherto unreported graft copolymer viz. graft copolymer (Sodium carboxymethylcellulose-g-*N*-vinylformamide) has prepared by employing peroxymonosulphate/thiourea redox system and to study some of the properties like swelling behavior, metal ion sorption and flocculation behaviours. The graft copolymer has been found to be thermally more stable than the parent backbone i.e. sodium carboxymethyl cellulose.

2. Experimental

2.1. Materials

N-vinylformamide (Aldrich) was distilled under reduced pressure at 14 mm and 55 °C and only middle fraction was used.

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Potassium peroxymonosulphate (Sigma), thiourea (E. Merck), and carboxymethylcellulose sodium salt (BDH, Pool) have been used as such. For maintaining hydrogen ion concentration, sulphuric acid (E. Merck) was used. All the solutions were prepared in triple distilled water. The other chemicals used are of analytical grade and used as such without further purification. For the flocculation, coking and non-coking coals were received from Steel Plant, Bokaro, India.

2.2. Procedure for graft copolymerization

For each experiment sodium carboxymethylcellulose solution has been prepared by slow addition of weighed amount of sodium carboxymethylcellulose to triple distilled water with rapid stirring in reactor. A calculated amount of *N*-vinylformamide (concentration from 12.0×10^{-2} to 12.0×10^{-2} mol dm^{-3}), thiourea (concentration from 1.2×10^{-2} to 4.4×10^{-2} mol dm^{-3}) and sulphuric acid solutions (concentration from 2.0×10^{-3} to 10.0×10^{-3} mol dm^{-3}) have been added into the reactor under the stream of oxygen free nitrogen gas. The reaction has been initiated by addition of known amount of deoxygenated potassium peroxymonosulphate solution (concentration from 4.0×10^{-3} to 12.0×10^{-3} mol dm^{-3}), after half an hour. After desired interval of time, the reaction has been stopped by letting air into the reactor. The grafted sample has been precipitated by pouring it into the water/ methanol mixture (ratio 1:5). The precipitate of graft copolymer has been separated, dried and weighed. To the filtrate a pinch of hydroquinone has been added and concentrated by distillation under reduced pressure. The poly (*N*-vinylformamide) has been precipitated by pouring the concentrated filtrate into pure acetone. The poly (*N*-vinylformamide) thus obtained has been separated, dried and weighed.

2.3. Estimation of grafting parameters

The graft copolymer has been characterized by following grafting parameters (Fanta, 1973a, 1973b).

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

$$\text{Grafting efficiency}(\%\ \text{E}) = \frac{\text{weight of grafted polymer}}{\text{weight of polymer formed}} \times 100$$

$$\text{Add on}(\%\ \text{A}) = \frac{\text{weight of synthetic polymer}}{\text{weight of graft copolymer}} \times 100$$

$$\text{Conversion}(\%\ \text{C}) = \frac{\text{weight of polymer formed}}{\text{weight of monomer charged}} \times 100$$

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

2.4. Method of characterization of sodium carboxymethyl cellulose/ sodium carboxymethyl cellulose-g-N-vinylformamide

2.4.1. IR spectroscopy

The IR spectra of sodium carboxymethylcellulose 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 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 *N*-vinylformamide (12×10^{-2}–28×10^{-2} mol dm^{-3}). 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 (Ps) has been calculated by using following expressions (Abd El-Rehim, Hegazy El-Sayed, & Ali, 2000).

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

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*-vinylformamide from 12×10^{-2} to 28×10^{-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 behavior of polymeric backbone and graft copolymer for five metals ions have been investigated by using following parameters (Rivas, Maturana, Molina, Glómez-Aantón, & Piérola, 1998).8).

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

$$\text{Partition coefficient}(K_d) = \frac{\text{amount of metal ion in the polymer}}{\text{amount of metal ion left in the solution}} \times \frac{\text{volume of solution(ml)}}{\text{weight of dry polymer}}$$

$$\text{Retention capacity}(Q_r) = \frac{\text{amount of metal ion in the polymer(m. Eq.)}}{\text{weight of dry polymer(g)}}$$

2.5.3. Flocculation

In 1.0 litre beaker, 200 cc of 1% wt. 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 ISO-TECH SYSTEM) to express the turbidity in nephelometric unit (N.T.U.).

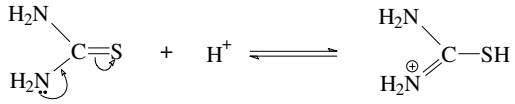
2.5.4. Determination of viscosity of polymer solutions

Viscosity was measured by using Ubbelhode capillary viscometer. During the measurement, temperature was maintained at 30 °C in thermostat. From efflux time of polymer solution (t) and that of solvent 1.0 M NaCl (t_o), relative viscosity $\eta_{rel} = \eta/\eta_0$ was obtained. Specific viscosity was calculated from the relationship $\eta_{sp} = \eta_{rel} - 1$. Knowing the concentration of polymer solution (C) in (g/dl), reduced viscosity was calculated for a set of five polymer concentrations. Intrinsic viscosity [η] was then obtained from common ordinate intercept on extrapolation of plots of reduced viscosity versus concentration.

3. Results and discussion

3.1. Mechanism

A tentative mechanism has been proposed on the basis of results obtained. Initially thiourea reacts with hydrogen ion to give protonated species, and this protonated species react with potassium peroxymonosulphate ($KHSO_5$) to form a complex, which dissociates to give primary free radicals $R_1S^{\cdot}$ and $SO_4^{\cdot}$ represented by $R_1^{\cdot}$. These radicals abstract hydrogen atom from the sodium carboxymethylcellulose molecules, producing sodium carboxymethylcellulose free radicals $Na-XO^{\cdot}$. The monomer molecules, which are in close vicinity of the reaction sites, become acceptor of carboxymethyl cellulose radicals resulting in chain initiation and thereafter themselves become free radical donor to neighboring molecules. In this way grafted chain grows. These grafted chains terminate by coupling to give graft copolymer. The probable reaction mechanism can be represented as-



Thiourea (R_1S) **Isothiourea (R_1SH)**

$$R_1SH + HSO_5^- \rightleftharpoons \text{Complex}$$

$$\text{Complex} \Longrightarrow R_1S^{\bullet} + H_2O + SO_4^{\bullet -}$$

Initiation

$$Na-XOH + R^{\cdot} \rightarrow Na-XO^{\cdot} + RH$$
$$M + R^{\cdot} \rightarrow RM^{\cdot}$$

where $R^{\cdot}$ = $R_1S^{\cdot}$ or $SO_4^{-\cdot}$, Na-XOH, sodium carboxymethylcellulose and M, monomer.

Propagation

$$Na\text{-}XO^{\cdot} + M \rightarrow Na\text{-}XOM_1^{\cdot}$$
$$Na\text{-}XOM_1^{\cdot} + M \rightarrow Na\text{-}XOM_2^{\cdot}$$
$$Na\text{-}XOM_2^{\cdot} + M \rightarrow Na\text{-}XOM_3^{\cdot}$$
$$\cdots$$
$$\cdots$$
$$Na\text{-}XOM_{n-1}^{\cdot} + M \rightarrow Na\text{-}XOM_n^{\cdot}$$
$$RM_1^{\cdot} + M \rightarrow RM_2^{\cdot}$$
$$RM_2^{\cdot} + M \rightarrow RM_3^{\cdot}$$
$$\cdots$$
$$\cdots$$
$$RM_{n-1}^{\cdot} + M \rightarrow RM_n^{\cdot}$$

Termination

$$Na-XOM_n^{\cdot} + Na-XOM_m^{\cdot} \rightarrow \text{Graft copolymer}$$
$$Na-XOM_n^{\cdot} + RM_n^{\cdot} \rightarrow \text{Graft copolymer}$$
$$RM_n^{\cdot} + RM_m^{\cdot} \rightarrow \text{Homopolymer}$$

3.2. Determination of optimum grafting conditions

The effect of the variation in concentration of potassium peroxymonosulphate (PMS), thiourea (TU), hydrogen ion (H^+), sodium carboxymethylcellulose (Na-CMC), *N*-vinylformamide (NVF) along with the effect of time and temperature on grafting parameters has been studied.

3.2.1. Effect of peroxymonosulphate concentration

The effect of potassium peroxymonosulphate (PMS) concentration on graft copolymerization of *N*-vinylformamide onto sodium carboxymethylcellulose has been studied by varying the concentration of peroxymonosulphate. The grafting ratio, add on, efficiency and conversion have been found to increase on increasing the concentration of PMS from 4.0×10^{-3} to 12.0×10^{-3} mol dm^{-3} and homopolymer formation decreases. The increment in grafting parameters may be due to the progressive reduction of peroxymonosulphate by thiourea, which produces primary free radicals i.e. $R^{\cdot} = R_1^{\cdot}$ and $SO_4^{\cdot -}$ (Mishra & Tripathy, 2008) and these primary free radicals generate more number of active sites on polymeric backbone, to which monomer addition takes place.

3.2.2. Effect of thiourea concentration

The variation of concentration of thiourea (TU) from 1.2×10^{-3} to 4.4×10^{-3} mol dm^{-3} reveals that of grafting ratio, add on, conversion and efficiency increase on increasing the thiourea concentration up to 3.6×10^{-3} mol dm^{-3} due to availability of more primary free radicals ($R^{\cdot} = R_1S^{\cdot}$ and $SO_4^{\cdot -}$, which might be formed due to reduction of PMS by thiourea. However, on further increasing the concentration of thiourea, the decrement in grafting parameters has been found which is probably due to premature termination of *N*-vinylformamide radicals giving rise to more homopolymer.

3.2.3. Effect of hydrogen ion concentration

The concentration of hydrogen ion plays an important role during the reaction. The effect of hydrogen ion concentration has been studied by varying the concentration from 2.0×10^{-3} to 10.0×10^{-3} mol dm^{-3}. It has been observed that grafting ratio, add on, conversion and efficiency increase due to protonation of thiourea (Tripathy, Mishra, Srivastava, Mishra, & Behari, 2008) which takes place on increasing the hydrogen ion concentration up to 6.0×10^{-3} mol dm^{-3}, which in turn protonated species reacts with PMS to give more primary free radicals.

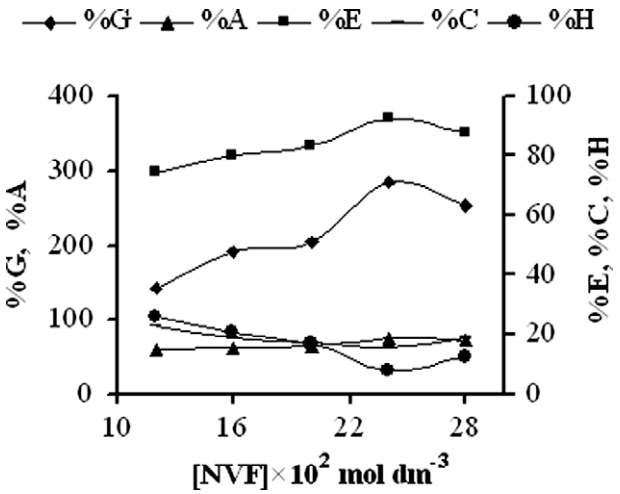
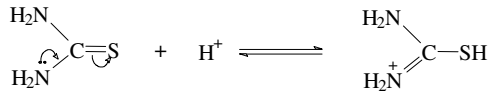


Fig. 1. Effect of *N*-vinylformamide concentration. [TU] = 2.8×10^{-3} mol dm^{-3}, [PMS] = 8×10^{-3} mol dm^{-3}, [CMC] = 1.0 g dm^{-3}, [H^+] = 6×10^{-3} mol dm^{-3}, Temperature = 35 °C, Time = 120 min.



Thiourea (R_1S) **Isothiourea (R_1SH)**

But on further increasing the concentration of [H^+] ions beyond 6.0×10^{-3} mol dm^{-3}, the grafting parameters decrease while homopolymer increases. It could be explained by following reasons

(1) It is due to premature termination of *N*-vinylformamide radicals giving rise to the formation of homopolymer.

(2) On increasing the hydrogen ion concentration, formation of H_2SO_5 species increases due to which concentration of HSO_5^- decreases resulting in production of less free radical, thereby decreasing the grafting parameters.

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

3.2.4. Effect of N-vinylformamide

The effect of concentration of *N*-vinylformamide on grafting parameters has been investigated by varying the concentration of *N*-vinylformamide (NVF) from 12.0×10^{-2} to 28.0×10^{-2} mol dm^{-3} and results are presented in (Fig. 1). It has been observed that grafting ratio, add on and efficiency increase on increasing the concentration up to 24×10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease. However the formation of homopolymer shows a reverse trend with respect to grafting efficiency. This behavior is attributed to accumulation of monomer at close proximity of polymeric backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of carboxymethylcellulose macro radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighboring. But on further increasing the concentration of *N*-vinylformamide, the results is found to decrease due to increased viscosity which facilitates the formation of homopolymer, which in turn hinders the movement of free radicals.

3.2.5. Effect of sodium carboxymethyl cellulose concentration

The effect of concentration of Na-carboxymethylcellulose (Na-CMC) has been observed with an aim to study the effect of its concentration (from 0.2 to 1.8 g dm^{-3}) on grafting parameters. It is obtained that the grafting parameters decrease continuously on increasing the concentration of sodium carboxymethylcellulose. This is due to the fact that as the concentration of sodium carboxymethyl cellulose increases, the viscosity of reaction medium increases, which hinders the movement of free radicals.

3.2.6. Effect of time

To investigate the effect of time on graft copolymerization, the reaction has been carried out by varying the duration of reaction from 60 to 180 min. It has been found that grafting ratio, add on, conversion and efficiency increase from 60 to 120 min. and thereafter, these parameters decrease. This is attributed due to propagation of grafting chains which takes place due to availability of more active species, which accounts for higher grafting. On further increasing the time interval beyond 120 min, all the active sites get exhausted as the mutual annihilation of growing grafted chains occurs, so that grafting parameters decrease.

3.2.7. Effect of temperature

The results obtained for all grafting parameters at different temperatures are observed on changing the temperature from 25 to

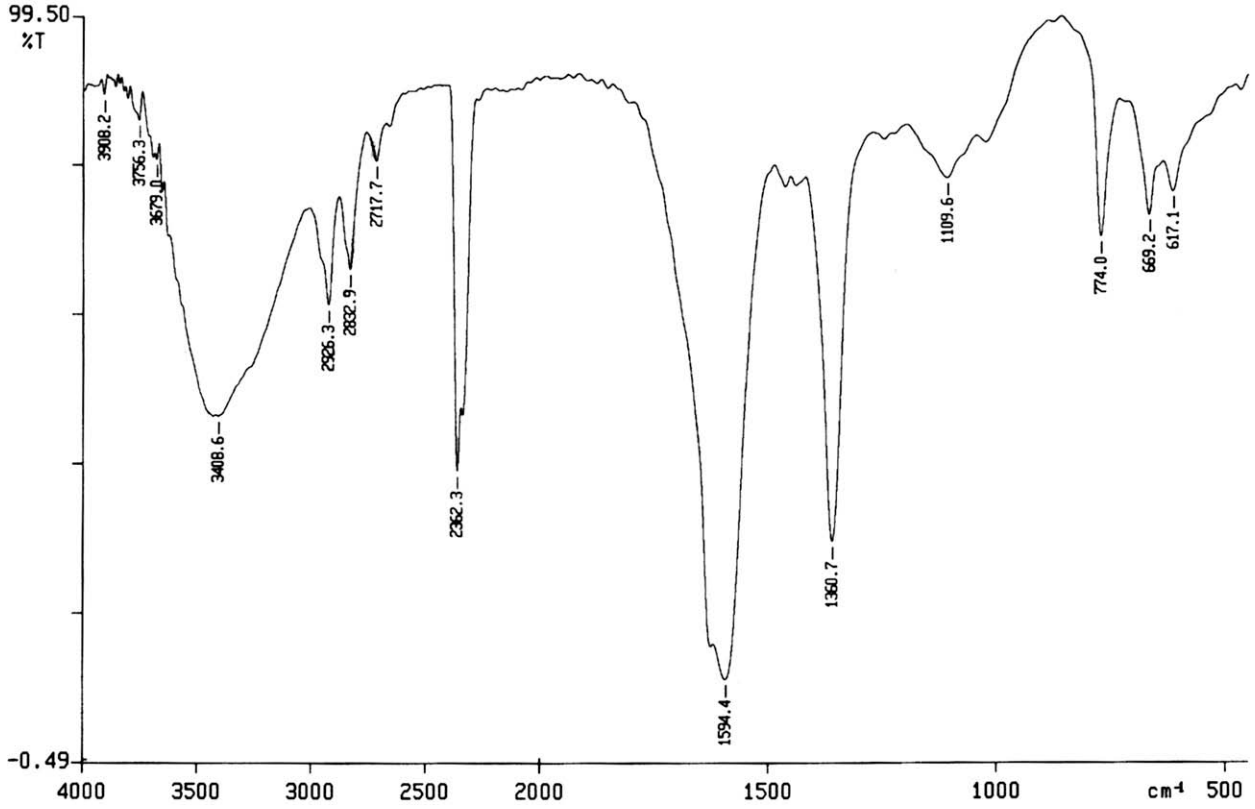


Fig. 2. IR spectrum of Na-Carboxymethyl cellulose concentration-g-*N*-vinylformamide.

45 °C, the grafting parameters increase up to 35 °C and there after decrease. The increment in grating parameters up to 35 °C is attributed due to the increase in the formation of active sites on account of enhanced production of primary free radicals with increase in temperature.

The decrement in grafting parameters could be explained as follows.

(1)It may be due to the premature termination of growing grafted chains by excess free radicals at higher temperature.

(2) Beyond the optimum value increase in temperature may lead to the decomposition of PMS into HSO_4^-, H_2O, O_2. Since O_2 acts as a scavenger for free radicals, which reacts with primary free radicals thereby lowering the free radical concentration.

4. Evidence of grafting

4.1. IR spectral analysis

On comparing the IR spectra of sodium carboxymethylcellulose and sodium carboxymethylcellulose-g-*N*-vinylformamide, it has been observed that a strong peak at 3430.6 cm^{-1} is observed due to OH stretching vibration in sodium carboxymethylcellulose. The spectrum of sodium carboxymethyl cellulose-g-*N*-vinylformamide (Fig. 2) shows variations in intensity and shifting of peak from 33430.6 to 3408.6 cm^{-1} appeared due to OH stretching vibration indicating the participation of hydroxyl in chemical reaction. The grafting of monomer is further confirmed by characteristic absorption band at 3679.0 cm^{-1} due to appearance of N–H stretching vibration (Amide II) of pendant chain of *N*-vinylformamide molecule results from the interaction between N–H bending vibration and –CN stretching vibration, respectively. A band at 1109.6 cm^{-1} is due to –CN stretching vibration of secondary amide present in pendant chain attached to sodium carboxymethylcellulose. The appearance of additional peaks due to the pendant chain of monomer in graft copolymer shifting of –OH stretching vibration suggest that grafting has been taken place on –OH sites of sodium carboxymethylcellulose.

4.2. Thermogravimetric analysis sodium carboxymethyl cellulose and Na-carboxymethylcellulose-g-N-vinylformamide

The polymer decomposition temperature (PDT) has been fount at about 120 °C. The rate of weight loss increases with increase in temperature from 125 to 200 °C and attains maximum at about 280 °C. It is single step degradation. $T_{max,}$ i.e. the temperature at which maximum degradation has been occurred, is found to be 287.0 °C. This is also confirmed by endothermic peak at about 300.0 °C appeared in DTA curve of sodium carboxymethylcellulose. The integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) have been found at about at 249 and 410.0 °C, respectively. About 19% char yield is obtained at 1000 °C. The weight loss at 125.0 °C is due to the loss of absorbed water. The graft copolymer began to degrade at about 140.0 °C. The polymer decomposition temperature (PDT) is found to be 155.0 °C. From thermogravimetric trace and differential thermal analysis curves of graft copolymer (presented in Figs. 3 and 4), it has been observed the degradations of it are in three-step processes i.e. in the range from 150.0 to 225.0 °C, from 255.0 to 390.0 °C and from 700.0 to 810.0 °C. Therefore three T_{max} are obtained at 175.0, 294.0 and 798.0 °C, respectively. The first two T_{max} are obtained due to loss of CO_2 and $-OCH_3$ groups (Scheme 1) respectively, while third T_{max} at 798.0 °C is due to loss of –NHCHO. The integral procedural decomposition temperature (IPDT) has been observed at about 311.0 °C. The final decomposition temperature (FDT) is found at about 812.0 °C which is higher than sodium carboxymethyl cellulose. A char yield of grafted sample is obtained at 900.0 °C. The higher value of FDT and IPDT indicates that graft copolymer is thermally more stable than sodium carboxymethyl cellulose.

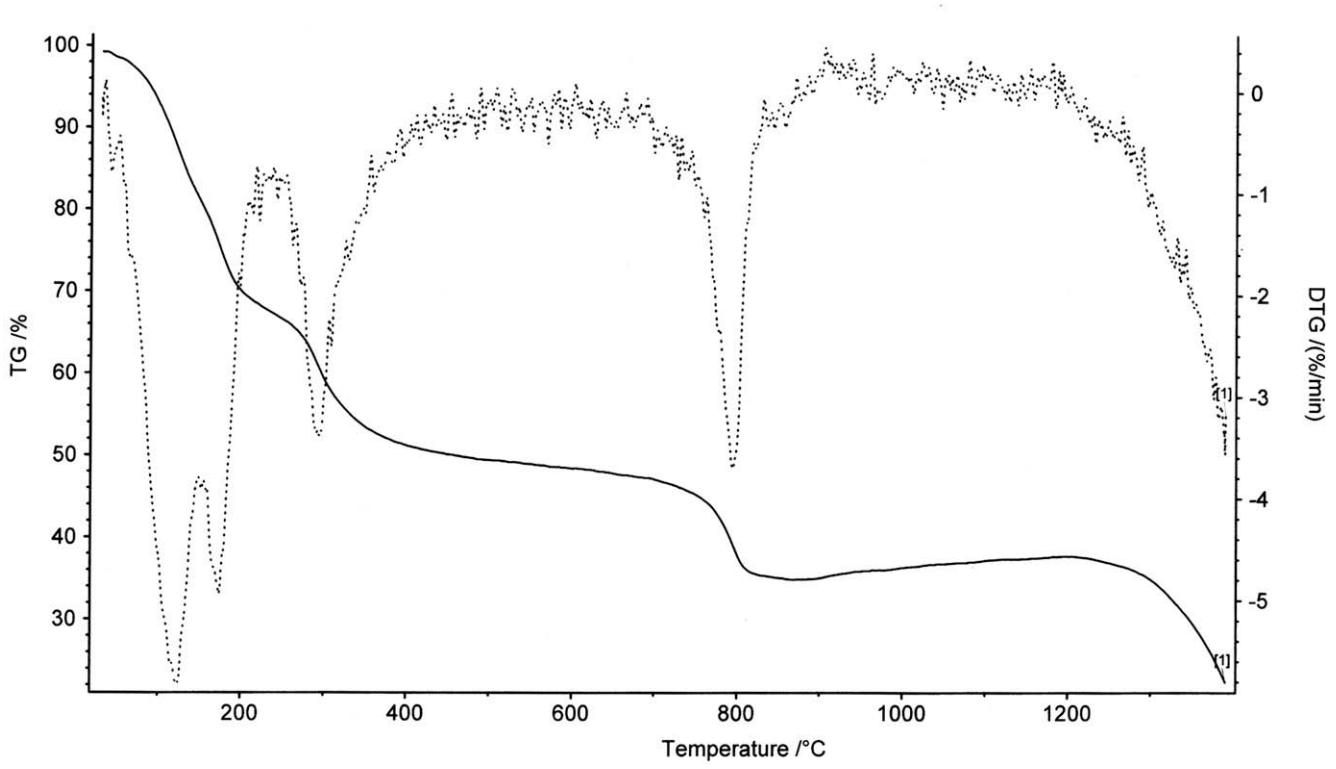


Fig. 3. Thermogravimetric analysis of Na-Carboxymethyl cellulose concentration-g-*N*-vinylformamide.

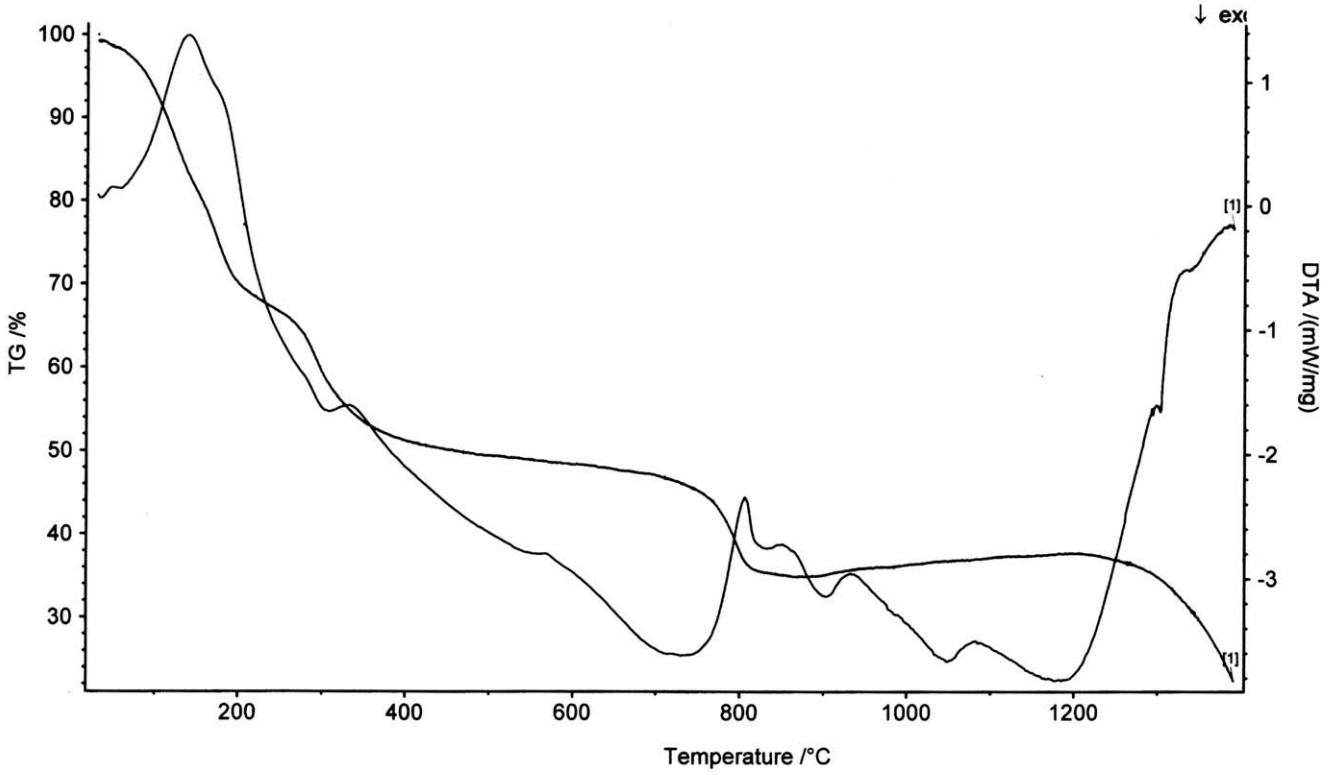
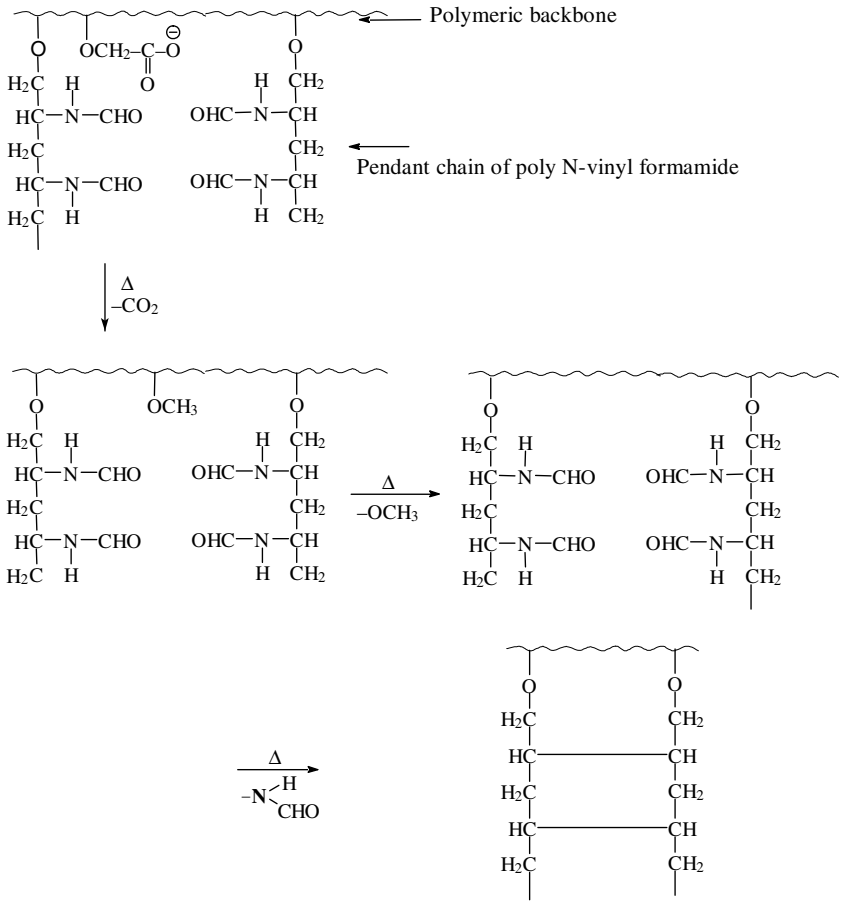


Fig. 4. Differential thermal analysis of Na-Carboxymethyl cellulose concentration-g-*N*-vinylformamide.



Scheme 1. Tentative presentation of degradation steps of graft copolymer.

Table 1
Swelling behaviour

Sample	[NVF] × 10^2 mol dm^{-3}	% G	Swelling ratio (S_r)	Percent swelling (P_s)
A	12	142	1.6	160
B	16	190	1.8	180
C	20	203	2.1	210
D	24	283	3.8	380
E	28	253	3.2	320

[PMS] = 8 × 10^{-3} mol dm^{-3}, [TU] = 2.8 × 10^{-3} mol dm^{-3}, Time = 120 min, [CMC] = 1.0 g dm^{-3}, [H^+] = 6 × 10^{-3} mol dm^{-3}, Temperature = 35 °C, where CMC = sodium carboxymethylcellulose, where A–E = Graft copolymer.

5. Study of the properties

5.1. Swelling test

An increase in weight of graft copolymer has been recorded by performing swelling test. The results have been summarized in Table 1, which indicates that swelling percent are dependent on concentration of monomer used while grafting. Since *N*-vinylformamide is a hydrophilic monomer, it increases the water retention character of graft copolymer. On increasing the concentration of *N*-vinylformamide grafting is increased, which may result into coiling network of poly (NVF), thus imbibes more water. The presence of carboxymethyl 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*-vinylformamide concentration, pendant chain of poly (*N*-vinylformamide) grows thereby increasing the swelling capacity of graft copolymer.

5.3. Metal ion sorption study

The results of sorption behavior of sodium carboxymethylcellulose and its grafted polymer with *N*-vinylformamide have been determined in terms of different parameters and the results are given in Table 2. 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 density of sorption sites for metal ions are increased due to availability of additional functional groups of poly pendent chain of monomer, which further increases with increased grafting. Results also show that Cu^{2+} was most uptakable in comparison to four metal ions of them, which have been used.

5.4. Flocculating properties

Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in (Fig. 5). It has been found that grafted copolymer (sodium carboxymethylcellulose-g-*N*-vinylformamide) gives better performance by showing lower turbidity than sodium carboxymethylcellulose itself. This phenomenon could be explained by considering bridging mechanism (Deshmukh, Singh, & Chaturvedi, 1985). In grafted copolymer, the dangling of poly (*N*-vinylformamide) chains have better approachability to the contaminant coal particles hence increases its flocculation capability. The difference in turbidity value in coking coal and non-coking coal in coal suspension is due to difference in negative charge density, which is higher in non-coking coal in aqueous solution (Gregory, 1982). Thus, by grafting of poly *N*-vinylformamide onto sodium carboxymethyl cellulose, efficient flocculants have been obtained and it could be used for the treatment of coal wastewater.

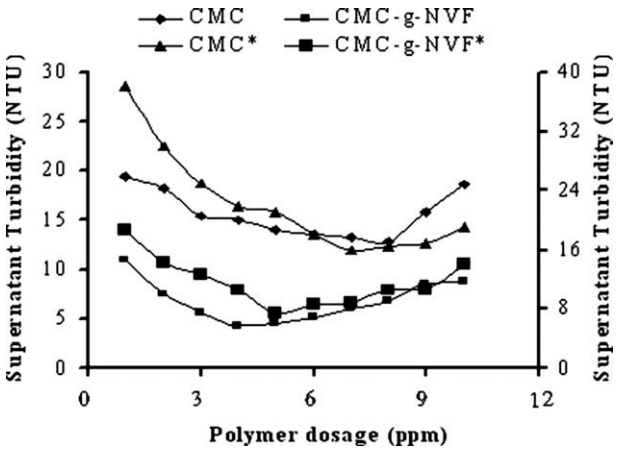


Fig. 5. Effect of polymer dosage on turbidity for coking and non-coking coal*.

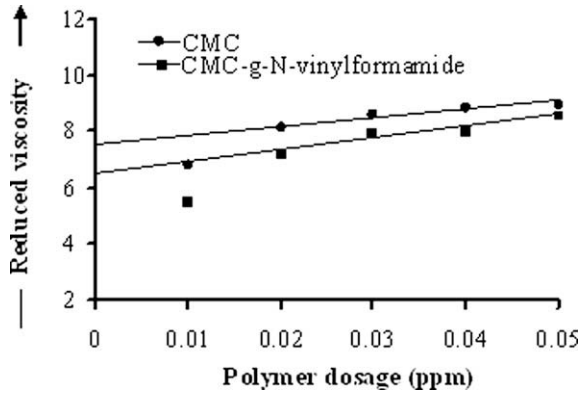


Fig. 6. Determination of intrinsic viscosity. [η] = 7.9 of Na-Carboxymethyl cellulose concentration and [η] = 6.5 of Na-Carboxymethyl cellulose concentration-g-*N*-vinylformamide.

Table 2
Metal ion sorption

Sample	[NVF] × 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+}
CMC	–	–	4.6	2.5	4.0	3.3	2.1	24.2	13.2	21.1	17.3	10.8	2.2	1.3	1.9	1.7	1.0
A	12	142	8.2	3.9	5.3	4.7	4.0	44.5	20.6	27.9	24.8	21.0	3.9	2	2.6	2.4	1.9
B	16	190	9.6	5.3	7.6	6.1	5.9	53.4	28.2	41.0	32.5	31.6	4.6	2.7	3.7	3.1	2.8
C	20	203	10.9	7.1	9.2	7.5	7.4	61.2	38.3	50.9	40.4	40.1	5.2	3.6	4.5	3.8	3.5
D	24	283	13.8	9.0	11.5	9.8	8.7	81.0	50.0	65.1	54.6	47.7	6.6	4.6	6.0	5.0	3.8
E	28	253	12.2	8.3	4.0	8.3	8.1	69.2	45.3	21.1	45.1	43.9	5.8	4.2	5.5	4.2	4.1

[PMS] = 8 × 10^{-3} mol dm^{-3}, [TU] = 2.8 × 10^{-3} mol dm^{-3}, Time = 120 min, [CMC] = 1.0 g dm^{-3}, [H^+] = 6 × 10^{-3} mol dm^{-3}, Temperature = 35 °C, where CMC = sodium carboxymethylcellulose, A–E = Graft copolymers.

5.5. Viscosity of polymer solutions

Intrinsic viscosity of sodium carboxymethylcellulose and sodium carboxymethylcellulose-g-*N*-vinylformamide is found to be 7.9 and 6.5, respectively, and results are presented in Fig. 6. The graft copolymer of *N*-vinylformamide shows lower intrinsic viscosity than sodium carboxymethylcellulose because longer grafted chains are available to make the molecule very flexible and thus reduces the viscosity drastically (Ungeheur, Bewersdorff, & Singh, 1989).

6. Conclusion

The thermal data show that the synthesized graft copolymer is thermally more stable than pure sodium carboxymethyl cellulose The synthesized graft copolymer i.e. sodium carboxymethylcellulose-g-*N*-vinylformamide shows better results for swelling, metal ion sorption and flocculating properties in comparison to sodium carboxymethylellulose, thus could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of *N*-vinylformamide might have taken place at hydroxyl group, 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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