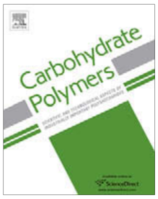
Carbohydrate Polymers 81 (2010) 97–103

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Preparation and characterization of modified sodium carboxymethyl cellulose via free radical graft copolymerization of vinyl sulfonic acid in aqueous media

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ARTICLE INFO

Article history:
Received 30 October 2009
Received in revised form 31 January 2010
Accepted 2 February 2010
Available online 6 February 2010

Keywords:
Graft copolymer
Potassium peroxydiphosphate
Thiourea
IR spectroscopy
Thermal analysis

ABSTRACT

The present paper reports the graft copolymerization of vinyl sulfonic acid onto sodium carboxymethyl cellulose by free radical polymerization using potassium peroxydiphosphate/thiourea redox system in an inert atmosphere. The reaction conditions for maximum grafting have been optimized by varying the concentration of vinyl sulfonic acid (2.6×10^{-2}–8.0×10^{-2} mol dm^{-3}), potassium peroxydiphosphate (4.0×10^{-2}–20×10^{-2} mol dm^{-3}), thiourea (0.8×10^{-3}–4.0×10^{-3} mol dm^{-3}), sulphuric acid (1.0×10^{-3}–6×10^{-3} mol dm^{-3}), sodium carboxymethyl cellulose (0.6–1.6 g dm^{-3}) along with time duration (60–180 min) and temperature (30–50 °C). Water swelling capacity, metal ion sorption, flocculation studies and resistance to biodegradability 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

The graft copolymerization of vinyl monomers onto natural and synthetic polysaccharides has received widespread attention in recent years (Fakhru'L-Razi et al., 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 vinyl sulfonic acid 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 (Kumar, Srivastava, & Behari, 2009; Tripathy, Mishra, Yadav, Sand, & Behari, 2009). Therefore sodium carboxymethylcellulose has been chosen a new type of polymeric backbone, which is water soluble cellulose ether. 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 carboxymethylcellulose has wide range of uses, but it suffers from a drawback i.e. biodegradability which limits its uses considerably. Poly (vinyl sulfonic acid, sodium salt) (PVSA) has negatively chargeable sulfonate groups and is a blood-compatible material. Many researchers (Kim, Park, & Kim, 2004) have reported that the incorporation of sulfonate groups into substrates reduces protein adsorption or platelet adhesion, due to the negatively charged character of these groups, in aqueous solutions. Lee and Oh (2002) reported that negatively chargeable sulfonate groups may be a very good candidate for a coating material for improved blood compatibility.

2. Experimental

2.1. Materials

Vinyl sulfonic acid (VSA) (Aldrich) has been purified by removing the inhibitor by partition method employing diethyl ether. Potassium peroxydiphosphate was received as a gift sample from FMC (United States), sodium carboxymethyl cellulose purchased from (Sigma, USA) and thiourea (E. Merck) were used as such. For maintaining hydrogen-ion concentration sulphuric acid (E. Merck) was used. The other chemical 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 Bokaro Steel Plant, India.

2.2. Procedure for grafting

For each experiment sodium carboxymethyl cellulose solution has been prepared by addition of weighed amount of sodium

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doi:10.1016/j.carbpol.2010.02.001

carboxymethyl cellulose into reactor containing triple distilled water with rapid stirring. A calculated amount of sodium carboxymethyl cellulose, vinyl sulfonic acid, sulphuric acid and thiourea 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 peroxydiphosphate 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. Thus grafted material precipitated, separated, dried and weighed. The poly vinyl sulfonic acid remained in the filtrate. To the filtrate a pinch of hydroquinone was added and concentrated by distillation under reduced pressure. The polymer of vinyl sulfonic acid was precipitated by pouring it into pure methanol, 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 vinyl sulfonic acid, 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 (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000).

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

$$P_S = S_R \times 100$$

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 vinyl sulfonic acid from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. For 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 sodium carboxymethyl cellulose and its grafted polymer with vinyl sulfonic acid have 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).

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

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

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

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 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.).

2.3.4. Resistance to biodegradability

Resistance to biodegradability of sodium carboxymethyl cellulose and sodium carboxymethyl cellulose-g-vinyl sulfonic acid has been measured in terms of viscosity and hence viscosity is calculated with the help of Ubbelohde capillary viscometer at constant temperature i.e. at 30 °C.

2.4. Characterization

2.4.1. FTIR analysis

The IR spectra of ungrafted 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. TGA/DTA analysis

The thermal analysis of sodium carboxymethyl cellulose and sodium carboxymethyl cellulose-g-vinyl sulfonic acid 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 optimum reaction conditions for maximum percentage of grafting have been established in the case of grafting of peroxydiphosphate, thiourea, vinyl sulfonic acid, sodium carboxymethyl cellulose (COH), sulphuric acid along with the temperature and time period.

3.2.1. Effect of peroxydiphosphate concentration

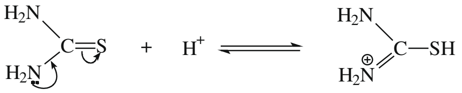
The effect of peroxydiphosphate concentration on graft copolymerization has been studied at different concentrations of peroxydiphosphate. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration of peroxydiphosphate from 4.0×10^{-3} to 20×10^{-3} mol dm^{-3} and the result have been summarized in Table 1. The increasing pattern has been found due to production of more primary free radicals R_1S° and $HPO_4^{\cdot -}$, which attack on the sodium carboxymethyl cellulose molecules creating more free radical sites onto which monomer addition takes place.

3.2.2. Effect of thiourea concentration

The effect of thiourea on grafting parameters has been studied by varying the concentration from 0.8×10^{-3} to 4.0×10^{-3} mol dm^{-3}. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration of thiourea up to 3.2×10^{-2} mol dm^{-3} but thereafter grafting parameters decrease. The increase in grafting parameters might be attributed to the increase in number of primary free radicals with increase in thiourea concentration up to a certain value. The decrease in these grafting parameters might be due to the premature termination of growing grafted chains.

3.2.3. Effect of hydrogen-ion concentration

The effect of the hydrogen-ion concentration on the grafting parameters was studied through the variation of the concentration of hydrogen ion from 2×10^{-3} to 6×10^{-3} mol dm^{-3}. The grafting ratio, add on, and efficiency increased when the hydrogen-ion concentration increased from 2×10^{-3} to 4×10^{-3} mol dm^{-3} but beyond this range, these parameters decreased. The increase in the grafting parameters with the hydrogen-ion concentration up to 4×10^{-3} mol dm^{-3} was due to protonation of TU, and these protonated species reacted with the active species of the PDP ion ($H_2P_2O_8^{-2}$) to give more primary free radicals; hence, an increase in the values of these parameters was observed:



However, beyond 5×10^{-3} mol dm^{-3}, these parameters decreased with an increase in the hydrogen concentration, and this was attributed to the formation of less active species (Bharadwaj, Sharma, & Gupta, 1976) of PDP such as $H_5P_2O_8^{+}$ and $H_6P_2O_8^{2+}$. The results are shown in Table 2.

3.2.4. Effect of vinyl sulfonic acid

The effect of concentration of vinyl sulfonic acid on grafting parameters has been investigated by varying the concentration of vinyl sulfonic acid from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. It has been observed that grafting ratio, add on and efficiency increase on increasing the concentration up to 5.3×10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease. However the formation of homopolymer shows a reverse trend with respect to grafting efficiency. This behaviour is attributed to accumulation of monomer molecules at close proximity of polymeric backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of sodium carboxymethyl cellulose macroradicals resulting in chain initiation and thereafter themselves become free radical donor to the neighboring molecules. But on further increasing the concentration of vinyl sulfonic acid, it is found that decrease in grafting parameter is observed which is due to increase viscosity of the medium, which in turn hinders the movement of free radicals.

Table 1
Effect of concentration of peroxydiphosphate.

[PDP] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
4	203.7	55.3	67.1	53.1	44.7
8	219.6	65.7	68.7	48.2	32.2
12	243.1	79.8	70.8	44.3	20.4
16	253.1	86.7	71.8	42.2	13.1
20	274.7	88.5	73.3	45.5	11.7

[VSA] = 5.3×10^{-2} mol dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, Time = 120 min, [CMC] = 1.0 g dm^{-3}, [TU] = 2.4×10^{-3} mol dm^{-3}, Temp. = 40 °C.

Table 2
Effect of concentration of hydrogen ion.

[H$^+$] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
2	196.8	70.3	66.3	40.6	29.7
3	217.2	74.1	68.4	42.5	25.9
4	243.1	79.5	70.8	44.3	20.4
5	221.6	78.9	73.5	40.8	21.1
6	190.8	76.1	65.6	36.5	23.6

[VSA] = 5.3×10^{-2} mol dm^{-3}, [PDP] = 12×10^{-3} mol dm^{-3}, Time = 120 min, [CMC] = 1.0 g dm^{-3}, [TU] = 2.4×10^{-3} mol dm^{-3}, Temp. = 40 °C.

3.2.5. Effect of sodium carboxymethyl cellulose concentration

The effect of concentration of sodium carboxymethyl cellulose has been observed with an aim to study the effect of its concentration (from 0.6 to 1.6 g dm^{-3}) on grafting parameters. It is observed that the grafting parameters decrease continuously with increasing the concentration of sodium carboxymethyl cellulose (Fig. 1). This might be due to the increase in the viscosity of reaction medium, which hinders the movement of free radicals.

3.2.6. Effect of time period

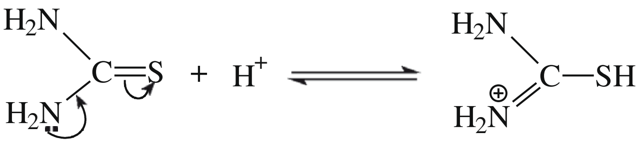
The effect of time duration on grafting reaction has been studied by varying the time period from 60 to 180 min. On increasing the time period from 60 to 120 min. the availability of more active species results into the increase in grafting ratio (%G = increases from 191.7 to 243.1), efficiency and add on. But further increase in time period, the decrement in these parameters (up to %G = 100) is observed which might be due to termination of growing grafted chains.

3.2.7. Effect of temperature

It has been observed that grafting ratio, add on and efficiency increase on increasing the temperature from 30 °C to 50 °C. The increment in grafting parameters is attributed to the increase in production of primary free radicals with consequent increase in number of grafting sites at polymer backbone and increase in rate of diffusion of poly (vinyl sulfonic acid) onto polymer backbone. These parameters have been decrease due to due the premature termination of growing grafted chains at higher temperature.

3.2.8. Mechanism

It is assumed that in the presence of hydrogen ion thiourea may be protonated which reacts with peroxydiphosphate (Bharadwaj et al., 1976) to give free radicals R_1S° and $HPO_4^{\cdot -}$. These radicals extract hydrogen atoms from sodium carboxymethyl cellulose molecules producing sodium carboxymethyl cellulose macro-free radicals. The monomer molecules which are in close vicinity of the reaction sites, become acceptor of sodium carboxymethyl cellulose radicals resulting in chain initiation and thereafter themselves become free radicals donor to neighboring molecules, thus grafted chain grows. Termination of chains by coupling yields graft copolymer. The tentative mechanism can be represented as



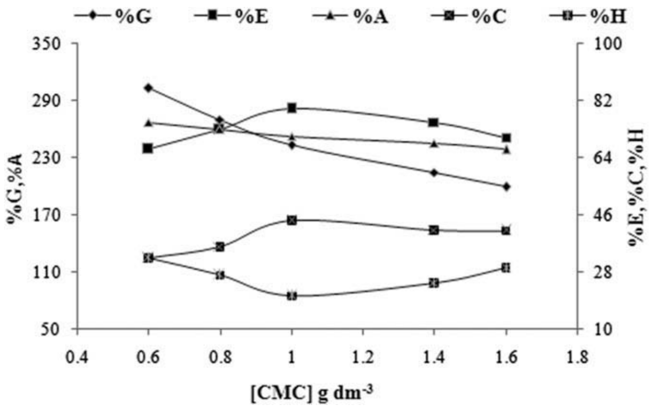


Fig. 1. Effect of concentration of sodium carboxymethyl cellulose [VSA] = 5.3×10^{-2} mol dm^{-3}, [PDP] = 12×10^{-3} mol dm^{-3}, Time = 120 min, [H$^+$] = 4×10^{-3} mol dm^{-3}, [TU] = 2.4×10^{-3} mol dm^{-3}, Temp. = 40 °C.

$$R_1SH + H_2P_2O_8^- \rightarrow R_1S^{\cdot} + H_2PO_4^- + HPO_4^{\cdot -}$$

Primary free radical $R^{\cdot} = R_1S^{\cdot}, \quad HPO_4^{\cdot -}$

Initiation

$$COH + R^{\cdot} \rightarrow CO^{\cdot} + RH$$

$$M + R^{\cdot} \rightarrow RM^{\cdot}$$

where COH = sodium carboxymethyl cellulose and M = vinyl sulfonic acid

Propagation

$$\begin{aligned} &COM_1^{\cdot} + M \rightarrow COM_2^{\cdot} \\ &COM_2^{\cdot} + M \rightarrow COM_3^{\cdot} \\ &\vdots \\ &COM_{(n-1)}^{\cdot} + M \rightarrow COM_n^{\cdot} \\ &RM_1^{\cdot} + M \rightarrow RM_2^{\cdot} \\ &\vdots \\ &RM_{n-1}^{\cdot} + M \rightarrow RM_n^{\cdot} \end{aligned}$$

Termination

$$COM_n^{\cdot} + COM_m^{\cdot} \rightarrow \text{ Graft copolymer}$$

$$COM_n^{\cdot} + CM_n^{\cdot} \rightarrow \text{Graft copolymer}$$

$$RM_n^{\cdot} + RM_m^{\cdot} \rightarrow \text{Homopolymer}$$

3.3. Evidence of grafting

3.3.1. IR spectroscopy of sodium carboxymethyl cellulose and sodium carboxymethyl cellulose-g-vinyl sulfonic acid

The IR spectra of ungrafted and grafted samples have been recorded with JASCO FTIR-5300 model in the range 500–4000 cm^{-1} to provide the proof of the grafting. Infrared spectrum of sodium carboxymethyl cellulose (Tripathy, Mishra, & Behari, 2009) showed strong peaks at 3444.9 cm^{-1} due to OH stretching vibrations. On comparing the IR spectra of sodium carboxymethyl cellulose and sodium carboxymethyl cellulose-g-vinyl sulfonic acid (Fig. 2), a band at 3454.4 cm^{-1} is appeared due to OH stretching vibration in the spectrum of sodium carboxymethyl cellulose-g-vinyl sulfonic acid. It is observed that there is variation in intensity of OH stretching vibration and shifting of this peak from 3444.9 to 3454.4 cm^{-1} in sodium carboxymethyl cellulose-g-vinyl sulfonic acid, indicating the participation of hydroxyl groups in grafting process. The graft copolymerization is further confirmed by characteristic absorption band of –SO$_2$–O– stretching vibration at 1183.4 cm^{-1} is due to presence of monomer molecule. The appearance of additional peaks in spectrum of graft copolymer and shifting of OH stretching vibration appeared in the spectrum of sodium carboxymethyl cellulose from the spectrum of sodium carboxymethyl cellulose-g-vinyl sulfonic acid showed that grafting might have taken place on OH sites of sodium carboxymethyl cellulose.

3.3.2. Thermal analysis of sodium carboxymethyl cellulose and sodium carboxymethyl cellulose-g-vinyl sulfonic acid

It has been observed that the degradation of sodium carboxymethyl cellulose (Srivastava and Behari, 2006) started at about 200 °C. The degradation has been found to occur in single step. The rate of weight loss increases with increase in temperature from 200 °C and attains a maximum at 286.5 °C and thereafter decreases and attains a constant value. About 60% of sodium carboxymethyl cellulose has been lost at 387.5 °C, therefore the final decomposition temperature (FDT) was not much high i.e. at 443.75 °C. The polymer decomposition temperature (PDT) has been found as 250 °C and temperature at which maximum degradation occur i.e. T_{max} has been found as 286.5 °C. This is also confirmed by endothermic peak at 297.9 °C which shows that maximum degradation has taken place within this temperature range. This T_{max} occured due to the loss of –CH$_2$COO$^-$ group of sodium carboxymethyl cellulose. In differential thermal analysis curve broad endothermic peak appeared with some fluctuation which shows the gradual degradation of polymeric backbone. Integral procedural decomposition temperature (IPDT) of sodium carboxymethyl cellulose has been found to be 237.19 °C and about 21.13% char yield occurs at 1000 °C. But in case graft copolymer the degradation of Sodium carboxymethyl cellulose-g-vinyl sulfonic acid (Fig. 3) starts to degrade at about 190.7 °C. The rate of weight loss increases with increase in temperature from 100.5 °C to 180.9 °C and attains maximum at 768.24 °C. Four T_{max} 262.50 °C, 324.11 °C, 768.24 °C and 1087.86 °C have been found due to four steps degradation. First T_{max} at 262.50 °C might be due to elimination of CO$_2$ molecule from the polymeric backbone, which is also confirmed exothermic peak present in DTA curve of graft copolymer at 270.56 °C. Second T_{max} at 324.11 °C might be due to elimination of –OCH$_3$ group from pendent chain attached to the polymeric back bone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 335.25 °C. The third T_{max} 768.24 °C at might be due to elimination of SO$_2$ molecule from pendent chain attached to the polymeric backbone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 775.21 °C. The fourth T_{max} 1087.86 °C at might be due to elimination of –OH group from pendent chain attached to the polymeric backbone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 1090.56 °C. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found to be at 1130.52 °C and 360.91 °C, respectively. The high value of Polymer decomposition temperature (PDT), final decomposition temperature (FDT), integral procedural decomposition temperature (IPDT) and three steps degradation indicate that graft copolymer is more stable than parent polymer backbone.

3.4. Properties

3.4.1. 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 660% occurs when grafting ratio is 250%. Since vinyl sulfonic acid is a

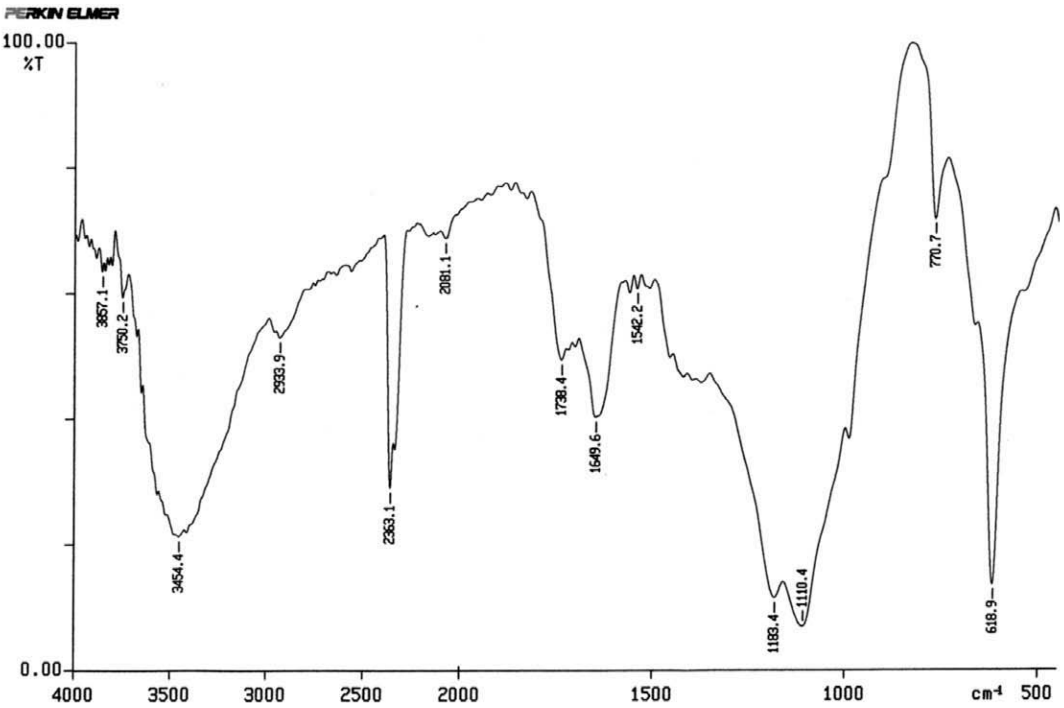


Fig. 2. IR spectrum of sodium carboxymethyl cellulose-g-vinyl sulfonic acid.

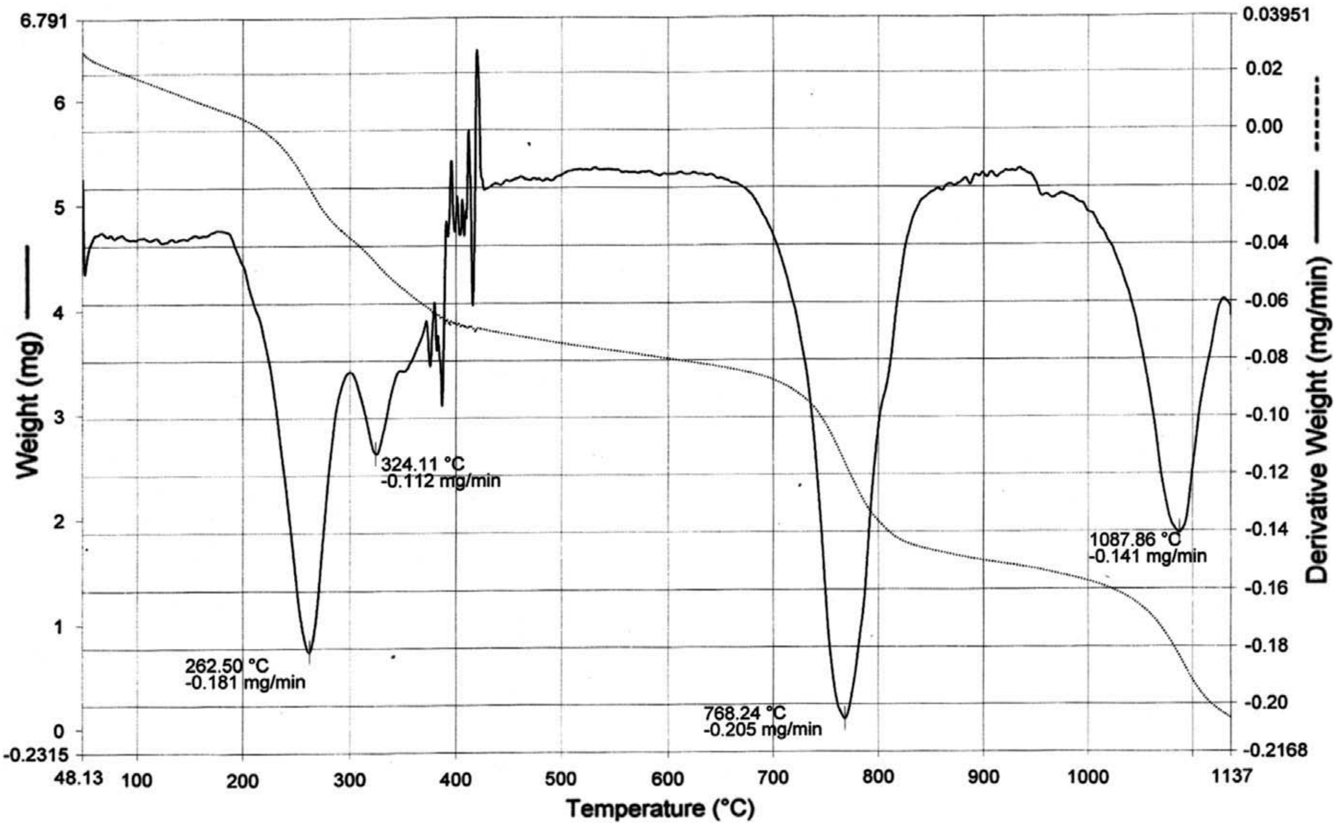


Fig. 3. Thermogravimetric trace of sodium carboxymethyl cellulose-g-vinyl sulfonic acid.

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 vinyl sulfonic acid chain, which coils and traps water molecules and thus helps in holding more water molecules.

Table 3
Metal ion sorption.

Sample	$[VSA] \times 10^2$ mol dm^{-3}	%G	Percent uptake (P_u)			Partition coefficient (K_d)			Retention capacity (Q_r)		
			Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
COH			2.7	2.3	1.2	13.7	11.2	7.3	1.5	1.3	0.7
A	2.6	177.7	3.1	2.9	1.7	17.7	13.2	8.2	1.8	1.6	0.9
B	4.0	229.7	6.2	5.1	3.4	32.4	26.2	20.7	3.7	3.2	2.3
C	5.3	243.1	7.2	6.2	5.2	42.3	35.2	21.2	4.2	3.8	2.9
D	6.6	333.4	10.3	9.7	8.7	56.3	55.6	48.5	5.5	5.1	4.7
E	8.0	205.7	10.2	11.5	10.7	70.2	61.2	56.2	6.0	5.7	5.8

$[VSA] = 5.3 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 4 \times 10^{-3}$ mol dm^{-3}, $[PDP] = 12 \times 10^{-3}$ mol dm^{-3}, Time = 120 min, $[CMC] = 1.0$ g dm^{-3}, $[TU] = 2.4 \times 10^{-3}$ mol dm^{-3}, Temp. = 40 °C.

3.4.2. Metal ion sorption behaviour of sodium carboxymethyl cellulose and its graft copolymer

The results of sorption behaviour of sodium carboxymethyl cellulose and its grafted polymer with vinyl sulfonic acid 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 3. 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. vinyl sulfonic acid and increment in sorption capacity takes place due to the incorporation of its pendant chain of poly (vinyl sulfonic acid), so higher the grafting, higher will be the sorption of metal ion. Results also show that Zn^{2+} was least uptakable in comparison to two metal ions, which have been used.

3.4.3. Flocculation performance

At the time of mixing, concentration of flocculants was very low so that to make a uniformly dispersed polymer solution and coal powder was uniformly suspended in the water by stirring. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone sodium carboxymethyl cellulose and graft copolymer of sodium carboxymethyl cellulose with vinyl sulfonic acid. 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 (sodium carboxymethyl cellulose-g-vinyl sulfonic acid) shows better performance than sodium carboxymethyl cellulose itself which could be explained due to the fact that in grafted copolymer, the dangling of poly (vinyl sulfonic acid) chains have better approachability (Deshmukh & Singh, 1987) to the contaminant coal particles. Here the bridging mechanism operates (Gregory, 1982), which involves binding or bridging individual particles to form flocs, hence increases its flocculation capability. By grafting of poly vinyl sulfonic acid onto sodium carboxymethyl cellulose, efficient flocculant has been obtained.

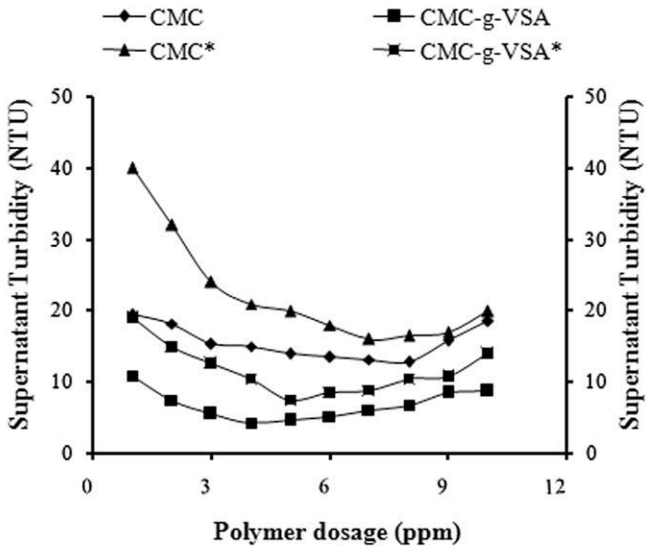


Fig. 4. Effect of polymer dosage on turbidity for coking coal and non-coking coal.

3.4.4. Resistance to biodegradability

From efflux time of polymer solution (t) and that of solvent 1.0 M $NaNO_3$ (t_0), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of sodium carboxymethyl cellulose-g-vinyl sulfonic acid is lower than sodium carboxymethyl cellulose (Fig. 5). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Singh, Deshmukh, & Chaturvedi, 1985). Sodium carboxymethyl cellulose solution, like other polysaccharide solutions, is highly prone to biodegradation, and it was found that its solution after 72 h of its preparation starts degrading and during 10 days the solution showed considerable loss of viscosity (Fig. 5, Line A). The graft copolymer solution was subjected for same type of study for biodegradation, and it has been observed that graft copolymer solution showed no loss of viscosity up to 10 days (Fig. 5, Line B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others (Ungeheur, Bewersdorff, & Singh, 1989). This is in an agreement with the fact that by incorporating relatively poly (vinyl sulfonic acid) chains in graft copolymer it can be made less susceptible to bacterial attack (Seaman, 1980).

Thus, it can be concluded that, by incorporation of poly (vinyl sulfonic acid) graft onto sodium carboxymethyl cellulose through graft copolymerization biodegradation can be minimized.

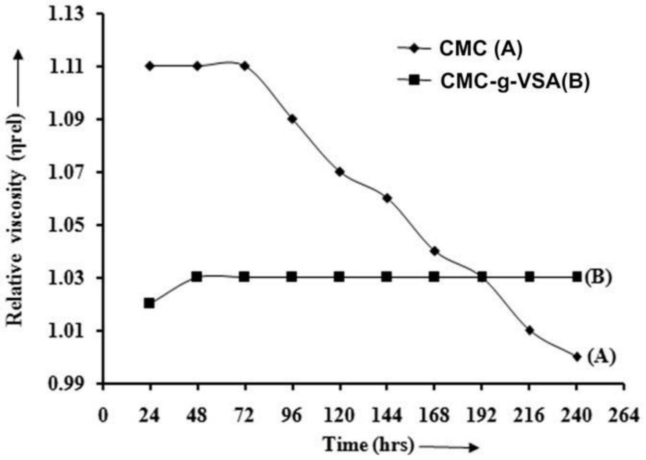


Fig. 5. Relative viscosity vs. time period to study biodegradation of sodium carboxymethyl cellulose and graft copolymer.

4. Conclusion

The spectroscopic data confirm that the grafting of vinyl sulfonic acid might have taken place at hydroxyl groups. The thermal analysis data show that the grafted polymer is more thermally stable than pure sodium carboxymethyl cellulose. Our synthesized graftcopolymer i.e. CMC-g-VSA shows better results for swelling, metal ion sorption, flocculation studies and resistance to biodegradation 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 financial support. Vide Project No. 37-393/2009 (SR).

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