Water soluble graft copolymer (κ-carrageenan-g-N-vinyl formamide): Preparation, characterization and application

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ABSTRACT

κ-Carrageenan-g-N-vinyl formamide was synthesized by free radical initiation using the potassium monopersulphate (PMS)/malonic acid redox pair in an inert atmosphere. The effects of variation of different reactant on grafting parameters have been studied by varying the concentration. Grafting ratio, add on and conversion showed an increasing trend on increasing the concentration of N-vinyl formamide, malonic acid, κ-carrageenan and the concentration of PMS from 6×10^{-3} to 22×10^{-3} mol dm^{-3}. The optimum temperature and time for grafting of N-vinyl formamide onto κ-carrageenan was found to be 40 °C and 120 min, respectively. The metal ion sorption, swelling behaviour, flocculation and resistance to biodegradation properties have been studied. Flocculation capability of κ-carrageenan and κ-carrageenan-g-N-vinyl formamide for both coking and non-coking coals has been studied for the treatment of coal mine waste water. The graft copolymer was characterized by FT-IR spectroscopy and thermogravimetric analysis.

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1. Introduction

Presently the industrial application of natural polymers and their derivatives is the most fascinating and vastly investigated field. For this purpose, biodegradable natural polymers such as polysaccharides and protein have been widely used (Jeong, Bae, Lee, & Kim, 1997; Younes & Cohn, 1987). One is κ-carrageenans; it is sulfonated anionic polygalactans extracted from marine red algae (Rees, Morris, Thorn, & Madden, 1982; Smidsrød & Grasdalen, 1982) (Rhodophyceae) mostly of genus Chondrus, Eucheuma, Gigartina and Iridaea. κ-Carrageenan is well differentiated with respect to disaccharide repeating units of alternating $(1 \rightarrow 3)$-α-ᴅ-galactose-4-sulphate and $(1 \rightarrow 4)$-β-3,6-anhydro-ᴅ-galactose residues (Harding, Day, Dhami, & Lowe, 1997; Layahe, 2001; Thanh et al., 2002). Carrageenan and its derivatives form valuable ingredients for foods, cosmetics and pharmaceuticals (Ruiter & Rudolph, 1997; Uruakpa, Arntfield, & LWT, 2006). In recent years, they have demonstrated to play significant role in antioxidant activities (Yuan et al., 2006; Zhang et al., 2003, 2004) and have been explored as effective excipients in controlled release drug delivery systems (Lazzarini, Maiorka, Liu, Papadopoulos, & Palermo-Neto, 2006; Makino, Idenuma, Murakami, & Ohshima, 2001). Even though, κ-carrageenan enjoys a number of applications, however, like other biopolymers, it also suffers from drawback like easier susceptibility of microbial attack and grafting provides an efficient route for removing this drawback. To date many investigations have been carried out on graft copolymerization reactions in view of preparing biopolymers based advanced materials. Reports on grafting of κ-carrageenan are scantly available (Pourjavadi, Harzandi, & Hosseinzadeh, 2004; Pourjavadi, Hosseinzadeh, & Mazidi, 2005) so, in the light of versatile applications of carrageenan and its derivatives, this work has been carried out with an aim to tailor κ-carrageenan based hybrid materials by grafting N-vinyl formamide.

N-vinyl formamide is a cationic hydrophilic monomer. With the availability of improved processes for synthesis and purification of N-vinyl formamide, poly(N-vinyl formamide) and its derivatives are widely used industrially (Pinschmidt et al., 1997). Poly(N-vinyl-formamide) has also been found to be an effective drag reducing agent (Marhefka, Marascalco, Chapman, Russell, & Kameneva, 2006). Prompted by the applications of N-vinyl formamide, hitherto unreported graft copolymer viz. graft copolymer (κ-carrageenan-g-N-vinyl formamide) has prepared by employing peroxymonosulphate/ malonic redox system and to study some of the properties like swelling behaviour, metal ion sorption, flocculation and resistance to biodegradability behaviour. The graft copolymer has been found to be thermally more stable than the parent backbone, i.e., κ-carrageenan.

2. Experimentals

2.1. Materials

N-vinyl formamide (Sigma Aldrich) has been used after distillation under reduced pressure of 14 mmHg at 55 °C in nitrogen atmosphere. Potassium peroxymonosulphate (Sigma) and malonic

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acid (Merck) have been used as such without further purification. κ-Carrageenan was purchased from Sigma Aldrich. For maintaining hydrogen ion concentration, sulphuric acid (Merck) has been used. Methanol has been used for precipitation. The other chemical reagents were of analytical grade. All the solutions were prepared in triple distilled water. For flocculation studies, coking and non-coking coal received from Bokaro steal plant, Bokaro (India) have been used.

2.2. Procedure for grafting

For each experiment, κ-carrageenan solution was prepared by slow addition of calculated amount of κ-carrageenan into reactor containing triple distilled water. A calculated amount of *N*-vinyl formamide, malonic acid and sulphuric acid solutions were added into the reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium peroxymonosulphate solution was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen free nitrogen gas at constant temperature. After desired time period, the reaction was stopped by letting air into reactor. The grafted sample was precipitated by pouring the reaction mixture into the water methanol mixture. The precipitate was separated, dried and weighed. The poly(*N*-vinyl formamide) remained in the filtrate.

2.3. Homopolymer separation

To the filtrate a pinch of hydroquinone was added and concentrated by distillation under reduce pressure. The poly(*N*-vinyl formamide) was precipitated by pouring the concentrated filtrate into pure methanol. The poly(*N*-vinyl formamide) thus obtained was separated, dried and weighed.

3. Study of properties

3.1. Swelling test

Swelling studies have been carried out with different grafted samples synthesized by varying the concentration of *N*-vinyl formamide. Each grafted sample (0.02 g) 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 using expression (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000).

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

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

3.2. Metal ion sorption test

The metal ion sorption study has been carried out by using samples of graft copolymers, which have been synthesized by varying the concentration of *N*-vinyl formamide from 8.0×10^{-2} to 24×10^{-2} mol dm^{-3}. For carrying this study, 0.02 g of graft copolymer has been taken in 10 ml of metal ion solution of known concentration, and kept for 24 h. The strength of sorbed metal ion has been determined by titrating the remaining metal ions. The results of sorption behaviour of κ-carrageenan and its grafted polymer with *N*-vinyl formamide has been determined in terms of

different parameters (Rivas, Maturana, Molina, Gomez-Anton, & Pierola, 1998), i.e., percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r).

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

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

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

3.3. Flocculation test

In 1.0 l beaker, 200 ml of 1 wt.% coal suspension was taken. The stirrer blade of the flocculator was dipped in the suspension. Under a low stirring condition, required quantity of polymer solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for half an hour. Clean supernatant liquid was withdrawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (supplied by ISO-TECH SYSTEM, India) to express the turbidity in nephelometric unit (N.T.U.).

3.4. Resistance to biodegradability

Resistance to biodegradability of κ-carrageenan and κ-carrageenan-g-*N*-vinyl formamide 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.

3.5. Characterization

3.5.1. FT-IR analysis
The infrared spectra analysis has been done to prove grafting. For this, the IR spectra of ungrafted and grafted samples in KBr pellets have been recorded with JASCO FT/ IR-5300 model in the range 500–4000 cm^{-1}.

3.5.2. TGA analysis
The thermal analysis of κ-carrageenan and *N*-vinyl formamide grafted κ-carrageenan has been carried in inert atmosphere at heating rate of 15 °C per minute within temperature range of 1400 °C on NETZSCH-STA 409 C/CD thermal analyzer.

4. Results and discussion

4.1. Grafting properties

The graft copolymer has been characterized as reported in the literature (Fanta, 1973a, 1973b).

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

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

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

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

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

4.2. Determination of optimum reaction conditions

The optimum reaction condition was obtained by varying the concentration of peroxymonosulphate (PMS), malonic acid (MA), sulphuric acid, N-vinyl formamide (NVF), κ-carrageenan (CgOH), along with reaction time and temperature and their effect on grafting parameters have been studied.

4.2.1. Effect of peroxymonosulphate concentration

The effect of potassium peroxymonopersulphate on grafting parameters has been studied by varying the concentration of PMS and the results are summarized in Table 1. It has been found that the grafting ratio, add on and conversion increase on increasing the concentration of peroxymonopersulphate (PMS) from 0.6×10^{-2} to 2.2×10^{-2} mol dm^{-3} (Table 1). This behaviour might be attributed due to progressive reduction of PMS by malonic acid producing primary free radicals (Mishra, Tripathy, & Behari, 2008), which attack on the κ-carrageenan molecules creating more active sites, to which monomer addition takes place.

4.2.2. Effect of malonic acid concentration

The effect of variation of malonic acid on graft copolymerization has been studied by varying its concentration from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3} and results are given in summarized Table 2. It has been observed that grafting parameters increase on increasing malonic acid concentration up to 3.2×10^{-3} mol dm^{-3} and thereafter grafting ratio, efficiency, add on and conversion decrease whereas homopolymer increases within this concentration range 3.2×10^{-3} to 4.8×10^{-3} mol dm^{-3}. This could be explained due to increase in number of primary free radicals (MA· and OH·, however, in high concentration of malonic acid, i.e., beyond 3.2×10^{-3} mol dm^{-3}, formation of poly(N-vinyl formamide) takes place, which decreases grafting efficiency and increases homopolymer percentage.

4.2.3. Effect of hydrogen ion concentration

To examine the effect of hydrogen ion concentration on graft copolymerization, the reaction has been carried at various concentrations of sulphuric acid, i.e., from 0.5×10^{-3} to 2.5×10^{-3} mol dm^{-3}. It has been found that the grafting ratio (%G = increases from 546.2 to 562.8), add on, and efficiency increase on increasing the concentration of hydrogen ion up to 1.5×10^{-3} mol dm^{-3}. However, beyond this concentration grafting ratio, add on, and efficiency decrease while conversion and homopolymer increases. This behaviour might be due to the formation

Table 1
Effect of peroxymonosulphate concentration.

[PMS] × 10^2 mol dm^{-3}	%G	%E	%A	%C	%H
0.6	198.9	69.1	66.5	25.3	30.8
1.0	399.6	75.7	79.9	46.3	24.2
1.4	562.8	85.0	84.9	58.2	14.9
1.8	763.3	76.2	88.4	88.0	23.7
2.2	908.3	71.7	90.0	111.2	28.2

[NVF] = 16×10^{-2} mol dm^{-3}, [CgOH] = 1.0 g dm^{-3}, [MA] = 3.2×10^{-3} mol dm^{-3}, [H$^+$] = 1.5×10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min.

Table 2
Effect of malonic acid concentration.

[MA] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
1.6	505.4	84.1	83.4	52.7	15.8
2.4	506.9	84.2	83.5	52.9	15.7
3.2	562.8	85.0	84.9	58.2	14.9
4.0	540.8	83.4	84.3	56.9	16.5
4.8	534.2	83.1	84.2	56.4	16.8

[NVF] = 16×10^{-2} mol dm^{-3}, [PMS] = 1.4×10^{-2} mol dm^{-3}, [CgOH] = 1.0 g dm^{-3}, [H$^+$] = 1.5×10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min.

of H$_2$SO$_5$ as an inactive species, thus the concentration of HSO$_5^-$ decreased resulting in less production of primary free radicals, which is responsible for decrease in the grafting parameters (%G = decreases from 562.8 to 545.0).

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

4.2.4. Effect of κ-carrageenan concentration

The graft copolymerization of N-vinyl formamide onto κ-carrageenan has been studied at different concentrations of κ-carrageenan. As the concentration of κ-carrageenan increased from 0.6 to 1.0 gm dm^{-3}, the grafting ratio (%G = increases from 488.5 to 562.8), add on and efficiency have been found to increase. This could be due to availability of more grafting sites with increasing concentration of κ-carrageenan. As the concentration of κ-carrageenan further increases the viscosity of the reaction medium increases, which hinders the movement of free radicals, thereby decreasing the grafting parameters (%G = decreases from 562.8 to 530.8).

4.2.5. Effect of N-vinyl formamide concentration

The effect of N-vinyl formamide (NVF) concentration on graft copolymerization has been studied by varying its concentration from 8×10^{-2} to 24×10^{-2} mol dm^{-3}. It has been observed that grafting ratio (%G = increases from 482.5 to 562.8), add on and efficiency increase on increasing the concentration of N-vinyl formamide (NVF) from 8×10^{-2} to 16×10^{-2} mol dm^{-3}. This increment might be explained due to greater availability of monomer molecules at the close proximity to the polymeric backbone. The monomer molecules, which are at immediate vicinity of reaction sites become acceptors of κ-carrageenan macroradicals (CgO·) resulting in chain initiation and thereafter themselves becomes free radical donor to neighbouring molecules leading to lowering of termination. But beyond 16×10^{-2} mol dm^{-3}, grafting parameters (%G = decreases from 562.8 to 522.5) decrease which might be attributed to increase in viscosity of reaction medium due to formation of homopolymer.

4.2.6. Effect of time period

The effect of change in duration of grafting reaction has been studied by varying the time interval from 60 to 180 min. It has been observed that grafting ratio (%G = increases from 510.5 to 562.8), efficiency and add on increase on increasing the time period from 60 to 120 min. On further increasing the time period, grafting parameters show decreasing trend. This behaviour may be explained due to the fact that, on increasing the time period propagation of grafting chains takes place due to availability of more macroradicals, which accounts for higher grafting, but on further increase in time interval, the mutual annihilation of growing grafted chains occur, which results in decrement of grafting parameters (%G = decreases from 562.8 to 504.1) and increment in homopolymer formation.

Table 3
Effect of temp.

| Temp. (°C)	%G	%E	%A	%C	%H
30	537.5	75.3	84.3	62.7	24.6
35	542.4	80.5	84.4	59.1	19.4
40	562.8	85.0	84.9	58.2	14.9
45	548.3	75.6	84.5	63.7	24.3
50	540.8	72.5	84.3	65.5	27.4

[NVF] = 16×10^{-2} mol dm^{-3}, [PMS] = 1.4×10^{-2} mol dm^{-3}, [MA] = 3.2×10^{-3} mol dm^{-3}, [CgOH] = 1.0 g dm^{-3}, [H$^+$] = 1.5×10^{-3} mol dm^{-3}, time = 120 min.

4.2.7. Effect of temperature

The effect of temperature on grafting parameters has been studied from 30 to 50 °C (Table 3). It has been observed that as the temperature is increased from 30 to 40 °C, there is an increase in value of grafting ratio, efficiency and add on. The increment in these grafting parameters up to 40 °C is due to the increment of production of primary free radicals, resulting in propagation of growing grafted chain. However, beyond 40 °C, there is decrement in grafting parameters which is supported by the fact that at higher temperature peroxymonosulphate PMS decomposes into HSO$_4^-$, H$_2$O, O$_2$. Since O$_2$ acts as a scavenger for free radicals, which reacts with primary free radicals thereby lowering the free radical concentration and resulting in the decrement in the grafting parameters.
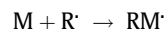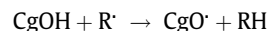
4.3. Mechanism

On the basis of experimental results, the probable reaction mechanism is suggested. Initially peroxymonosulphate interacts with malonic acid to form free radicals R·, which may abstract hydrogen atom from κ-carrageenan and thereby producing (CgO·) macroradicals. The malonic acid molecules which are in close vicinity of the reaction sites become acceptors of κ-carrageenan radicals resulting in chain initiation of graft copolymer and thereafter themselves become free radical donor to neighbouring molecules. In this way grafted chains grow. These chains are terminated by coupling to give graft copolymer. The tentative mechanism is given as follows:
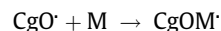
$$\underset{\text{MA}}{CH_2(COOH)_2} + \underset{\text{PMS}}{HSO_5^-} \rightarrow \underset{\text{MA·}}{CH^·(COOH)_2} + H_2O + SO_4^{·-}$$
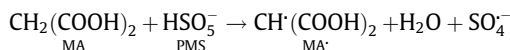
R· represent MA· and SO$_4^{·-}$

Initiation:

$$CgOH + R^· \rightarrow CgO^· + RH$$
$$M + R^· \rightarrow RM^·$$

where CgOH = κ-carrageenan, M = monomer

CgO·(Macroradical)

Propagation:

$$CgO^· + M \rightarrow CgOM^·$$
$$CgOM^· + M \rightarrow CgOM_1^·$$
$$\cdots\cdots\cdots$$
$$\cdots\cdots\cdots$$
$$\cdots\cdots\cdots$$
$$CgOM_{n-1}^· + M \rightarrow CgOM_n^·$$
$$RM^· + M \rightarrow RM_1^·$$
$$RM_1^· + M \rightarrow RM_2^·$$
$$\cdots\cdots\cdots$$
$$\cdots\cdots\cdots$$
$$\cdots\cdots\cdots$$
$$RM_{n-1}^· + M \rightarrow RM_n^·$$

Termination:

$$CgOM_n^· + CgOM_m^· \rightarrow \text{Graft copolymer}$$
$$RM_n^· + CgOM_n^· \rightarrow \text{Graft copolymer}$$
$$RM_n^· + RM_m^· \rightarrow \text{Homopolymer}$$
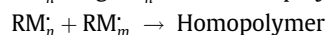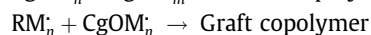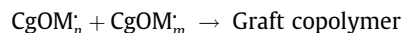
4.4. Evidence of grafting

4.4.1. IR spectroscopy analysis of κ-carrageenan and grafted κ-carrageenan-g-N-vinyl formamide

The infra red spectra analysis has been utilized to prove grafting, for this IR spectra of κ-carrageenan-g-N-vinyl formamide, (Fig. 1) have been recorded in the range of 500–4000 Cm^{-1}. On comparing the IR spectra of κ-carrageenan (Mishra et al., 2008) and κ-carrageenan-g-N-vinyl formamide, a broad band near at 3504.6 cm^{-1} is due to OH stretching vibration in the spectrum of κ-carrageenan is shifted from 3504.6 to 3213.4 cm^{-1} in κ-carrageenan-g-N-vinyl formamide , indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band at 1678.5 cm^{-1} due to >C=O stretching vibration and amide (II) results from the interaction between N–H bending vibration and —CN stretching vibrations, respectively, along with characteristic absorption band at 3772.7 cm^{-1} due to the appearance of N–H stretching vibration of amide (II) in graft copolymer. A band at 1112.3 cm^{-1} is appeared due to C–O–C stretching vibration and C–N stretching vibration of secondary amide of monomer (N-vinyl formamide), respectively. The appearance of additional peaks in spectrum of graft copolymer due to attachment of N-vinyl formamide and shifting of OH in plane bending vibration appeared in the spectrum of κ-carrageenan at 1377.1 to 1399.9 cm^{-1} in spectrum of κ-carrageenan-g-N-vinyl formamide showed that grafting might have been taken place on OH sites of κ-carrageenan.

4.4.2. Thermogravimetric analysis of κ-carrageenan and grafted κ-carrageenan-g-N-vinyl formamide

4.4.2.1. κ-Carrageenan. Thermogravimetric analysis curve of carrageenan has been taken from our publication (Mishra et al., 2008). The 10% weight loss has been found at about 106.2 °C which may be due to loss of absorbed water. The degradation of κ-carrageenan has started at about 135 °C. It is single step degradation. The polymer decomposition temperature (PDT) has been found at 150 °C. The rate of weight loss increases at a particular temperature, i.e., 212.5 °C at which degradation has occurred, and thereafter the weight loss decreases gradually. $T_{max,}$ the temperature at which maximum degradation occurs, is 212.5 °C, which is also confirmed by endothermic peak present in κ-carrageenan DTA curve (Mishra et al., 2008) at about 219.2 °C. However, the weight loss 58.5% has been found at 700 °C. The Final decomposition temperature (FDT) is at about 800 °C. The Integral procedural decomposition temperature (IPDT) of κ-carrageenan has been found to be 253.3 °C.

4.4.2.2. κ-Carrageenan-g-N-vinyl formamide. The degradation of graft copolymer (κ-carrageenan-g-N-vinyl formamide) starts at about 89.8 °C. The weight loss of 10% at 187.5 °C is due to the loss of absorbed water. The polymer decomposition temperature (PDT) has been found at 207.2 °C. The rate of weight loss increases with increase in temperature from 150 °C to 800 °C and thereafter attains a maximum at about 1295.5 °C. The degradation of graft copolymer (κ-carrageenan-g-N-vinyl formamide) occurs in more than one step, i.e., between 300–350, 750–800 and 1270–1320 °C, respectively. Three T_{max} 311.7, 782.8 and 1295.3 °C have been found due to three step degradation. First T_{max} at 311.7 °C might be due to elimination of —OSO$_3^-$ from the polymeric backbone. Second T_{max} at 782.8 °C might be due to elimination of –CO
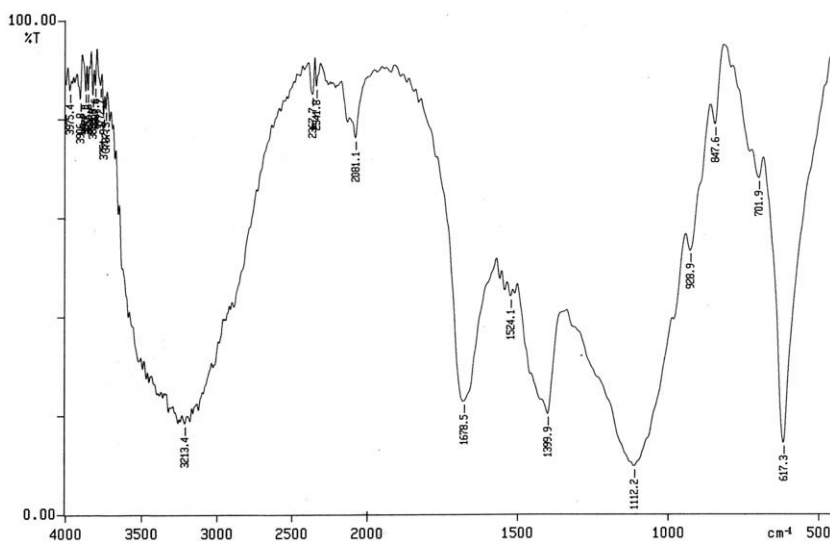
Fig. 1. IR spectrum of κ-carragenan-g-*N*-vinyl formamide.

group from pendent chain attached to the polymeric back bone. The third T_{max} 1295.3 °C at might be due to elimination of $–NH_3$ molecule from pendent chain attached to the polymeric backbone. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found to be at 1295.3 and at 315.1 °C, respectively. The high value of Polymer decomposition temperature (PDT), final decomposition temperature (FDT), integral decomposition temperature (IPDT) and three steps degradation indicate that graft copolymer is more stable than parent polymer backbone. Thermogravimetric analysis trace of κ-carrageenan-g-*N*-vinyl formamide are presented in Fig. 2.

4.5. Properties

4.5.1. Swelling capacity

The results of swelling studies reveal that swelling of graft copolymer is dependent upon percent grafting. Since the increment in percent grafting is directly related with monomer concentration, thus water retention capacity and hydrophilicity is increased with increase in concentration of monomer, i.e., vinyl formamide. It has been observed that a maximum percent swelling

of 302% is obtained when grafting ratio is 522%. With the increase in percent grafting, length of pendent of poly(vinyl formamide) increases which helps in holding more water, thereby increasing the swelling capacity of graft copolymer.

4.5.2. Metal ion sorption ability of κ-carrageenan and its graft copolymer

The result of sorption behaviour of κ-carrageenan and its grafted polymer with vinyl formamide has been determined in terms of percent ion uptake (P_u), partition coefficient (K_d), retention capacity (Q_r). The results are summarized in Table 4, which depicts 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, pendent chain of poly(vinyl formamide) increases, which offers additional sites for metal ion sorption. Thus with the incorporation of more functional groups of polyvinyl formamide, number of sorption sites increase, thereby enhancing the sorption capacity of grafted κ-carrageenan as compared to the ungrafted carrageenan. The order of selectivity of sorption of metal ions is $Pb^{2+} > Ni^{2+} > Zn^{2+}$.
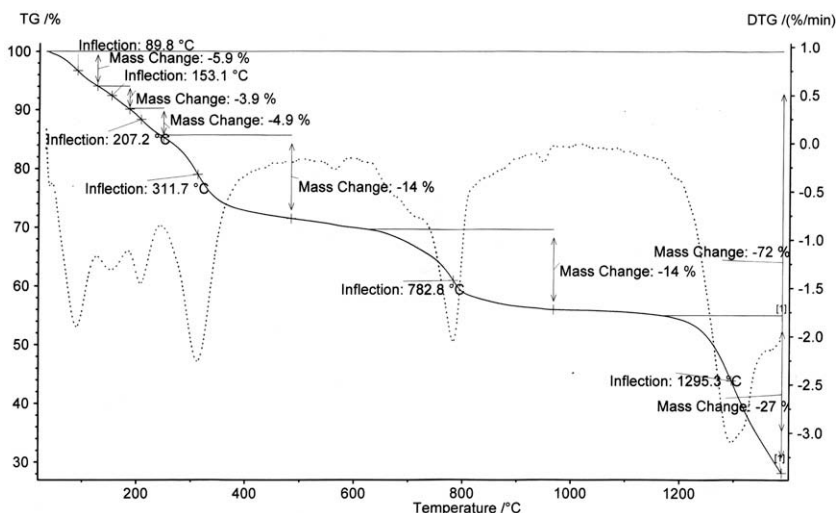

Fig. 2. Thermogravimetric trace of κ-carragenan-g-*N*-vinyl formamide.

Table 4
Metal ion sorption.

Sample	$[NVF] \times 10^2$ mol dm^{-3}	%G	Percent uptake (P_u)			Partition coefficient (K_d)			Retention capacity (Q_r)		
			Pb^{2+}	Ni^{2+}	Zn^{2+}	Pb^{2+}	Ni^{2+}	Zn^{2+}	Pb^2	Ni^{2+}	Zn^{2+}
CgOH	–	–	4.1	2.1	1.8	10.8	5.4	4.8	1.0	0.5	0.5
A	8	482.5	10.4	4.2	3.7	29.0	11.1	9.8	2.5	1.0	1.0
B	12	500.2	14.5	6.3	5.6	42.6	17.0	15.0	3.5	1.5	1.5
C	16	562.8	27.0	12.7	11.3	92.8	36.5	31.9	6.5	3.0	3.0
D	20	543.7	22.9	10.6	9.4	74.3	29.7	26.0	5.5	2.5	2.5
E	24	522.5	18.7	8.5	7.5	57.6	23.2	20.4	4.5	2.0	2.0

Where CgOH = κ-carrageenan and A–E = graft copolymers.
[CgOH] = 1.0 g dm^{-3}, [PMS] = 1.4 × 10^{-2} mol dm^{-3}, [MA] = 3.2 × 10^{-3} mol dm^{-3}, [H$^+$] = 1.5 × 10^{-3} mol dm^{-3}, temp. = 40 °C, time = 120 min.
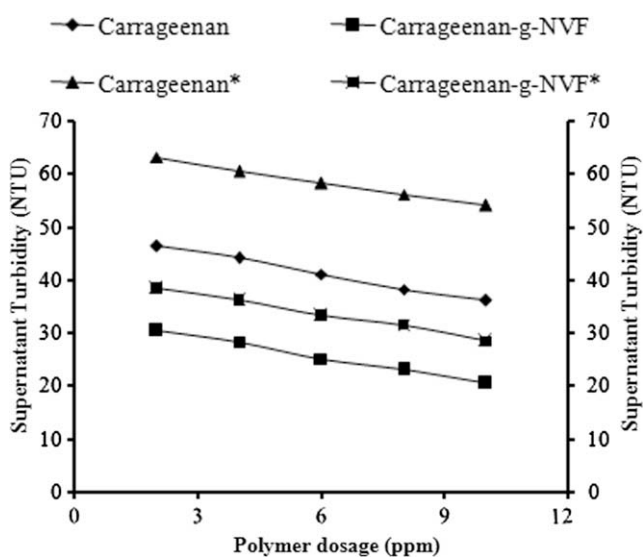
Fig. 3. Effect of polymer dosage on turbidity for coking coal and non-coking coal.

Fig. 4. Resistance to Biodegradability of κ-carrageenan and its graft copolymer (κ-carragenan-g-N-vinyl formamide).

4.5.3. Flocculation performance

Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are given in Fig. 3. It has been found that grafted copolymer (κ-carrageenan-g-N-vinyl formamide) gives better performance by showing lower turbidity than κ-carrageenan itself. This phenomenon could be explained by considering bridging mechanism (Bratby, 1980, Chap. 8; Deshmukh, Singh, & Chaturvedi, 1985) In grafted copolymer, the dangling of poly(N-vinyl formamide) 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-vinyl formamide) onto κ-carrageenan, efficient flocculants have been obtained and it could be used for the treatment of coal wastewater.

4.5.4. Resistance to biodegradability of κ-carrageenan and its graft copolymer

The results presented in the form of graph in (Fig. 4). From efflux time of polymer solution (t) and that of solvent 1.0 M NaNO₃ (t_0), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of κ-carrageenan-g-N-vinyl formamide is lower than κ-carrageenan (Fig. 4). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Ungeheur, Bewersdorff, & Singh, 1989). κ-Carrageenan 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. 4, 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. 4, Line B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others (Deshmukh & Singh, 1987). This is in an agreement with the fact that by incorporating relatively poly(N-vinyl formamide) chains in graft copolymer it can be made less susceptible to bacterial attack (Seaman, 1980).
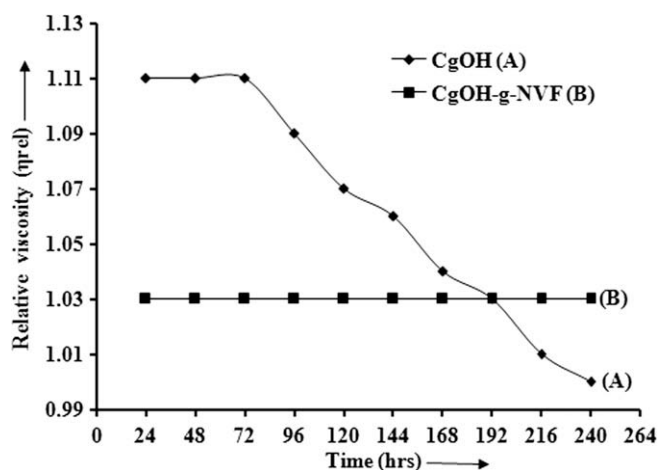
Thus, it can be concluded that, by incorporation of poly(N-vinyl formamide) graft onto κ-carrageenan through graft copolymerization, the drag reduction effectiveness can be enhanced and biodegradation can be minimized.

5. Conclusions

The spectroscopic data confirm that the grafting of vinyl formamide has occurred at hydroxyl group of κ-carrageenan molecule. The thermal analysis data show that the grafted polymer is more thermally stable than ungrafted polymer (considering both higher final decomposition temperature and integral procedural decomposition temperature of the grafted polymer as compared to substrate). Grafted polymer shows very good water swelling ability and resistance to biodegradability. Grafting is further supported by enhanced properties like metal ion uptake and flocculation efficiency.

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