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Free radical graft copolymerization of N-vinyl-2-pyrrolidone onto k-carrageenan in aqueous media and applications

Madan Mohan Mishra[a], Arpit Sand[a], Dinesh Kumar Mishra[b], Mithilesh Yadav[a], Kunj Behari[a,*]

[a] Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India
[b] Polymer Science & Engineering Division, National Chemical Laboratory, Dr. Homibhabha Road (Pashan), Pune, 411008, India

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ABSTRACT

In the present article, the graft copolymer of k-carrageenan with N-vinyl-2-pyrrolidone (NVP) has been synthesized using PMS/maleic acid as a redox initiator in aqueous medium and reaction conditions have been optimized to obtain maximum % grafting ratio (%*G*). The optimum conditions of maximum grafting have been found by varying the different parameters. On increasing the concentration of maleic acid and peroxymonosulphate from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3} and 0.6×10^{-2} to 2.2×10^{-2} mol dm^{-3} respectively, the initially grafting parameters increased and after a certain range of concentration grafting parameters showed decreasing trend. The small increment of concentration in hydrogen ion causes increment in percentage grafting. It was observed that the grafting parameters increase as the concentration of N-vinyl-2-pyrrolidone increases up to 16×10^{-2} mol dm^{-3} after that it decreased. The optimum condition for maximum grafting has obtained at concentration 1.0 g dm^{-3}of k-carrageenan at 40 °C and 120 min, respectively.

1. Introduction

Now-a-days more emphasis is given to biodegradable polymers such as polysaccharides and proteins, which have been extensively used and investigated for industrial applications. In our laboratory, by the process of grafting, physico-chemical properties of synthetic monomers are superimposed onto the properties of different natural polymers (Kumar, Srivastava, Behari, 2009; Tripathy, Mishra, & Behari, 2009; Tripathy, Mishra, Yadav, Sand, & Behari, 2009). Due to the exceptional properties, i.e. biodegradability, renewability, biocompatibility, nontoxicity and wide availability, polysaccharides are constituted the main skeleton of these new materials. The functional groups of these natural polymers offer sites to add special properties by grafting-desired monomers and thus enlarge their potential applications without affecting the fundamental properties of natural polymers (Mishra, Tripathy, & Behari, 2008; Srivastava & Behari, 2006). k-Carrageenan is sulphated anionic polygalactans extracted from marine red algae (Smidsrød & Grasdalen, 1982; Rees, Morris, Thorn, & Madden, 1982) (Rhodophyceae) mostly of genus Chondrus, Eucheuma, Gigartina, and Iridaea. The carrageenan family has three main branches named kappa, iota, lambda, which are well differentiated with respect to disaccharide-repeating units of alternating (1 → 3)-α-D-galactose-4-sulphate and (1 → 4)-β-3,6-anhydro-D-galactose residues (Harding, Day, Dhami, & Lowe, 1997; Layahe, 2001; Thanh et al., 2002). Carrageenans and their derivatives form valuable ingredients for foods, cosmetics, and pharmaceuticals (Ruiter & Rudolph, 1997; Uruakpa, Arntfield, & LWT, 2006). Carrageenan oligomers have been reported to have anti-HIV (Human Immuno deficiency Virus) activities (Yamada, Ogamo, Saito, Uchiyama, & Nakagawa, 1997; Yamada, Ogamo, Saito, Uchiyama, & Nakagawa, 2000). In recent years, they have been demonstrated to play significant role in antioxidant activities (Yuan et al., 2006; Zhang et al., 2003) and explored as effective excipients in controlled release drug delivery systems (Makino, Idenuma, Murakami, & Ohshima, 2001; Zhang et al., 2004). However, k-carrageenan enjoys a number of applications, like other biopolymers, it also suffers from drawback like easier susceptibility of microbial attack and grafting provides an efficient route for removing this drawback. Upto date many investigations have been carried out on graft copolymerization reactions in view of preparing biopolymers-based advanced materials. Reports on grafting of k-carrageenan are scantly available (Pourjavadi, Harzandi, & Hosseinzadeh, 2004; Pourjavadi, Hosseinzadeh, & Mazidi, 2005) so, in the light of versatile applications of carrageenan and its derivatives. The N-vinyl-2-pyrrolidone (NVP) monomer is a hydrophilic and nontoxic in nature. A kind of compound which plays an important function in many fields, such as paints and coatings, ink, cosmetic and pharmaceuticals (Duan, 1993; Gaenger & Florig, 2007; Suzuki, Fukuda, & Yoneto, 2003). Homopolymer and copolymer of N-vinyl-2-pyrrolidone have been

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* Corresponding author. Tel.: +91 9005807357.
E-mail address: sand.arpit@gmail.com (K. Behari).

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used as an antimicrobial agent in clinical practice (Nud'ga et al., 2002) and also as the main component of temporary skin covers (O'Connell et al., 2001) and wound dressings (Nho & Park, 2002). Therefore, their properties and versatile applications aforementioned, prompted us to synthesize the hitherto unreported graft copolymer of k-carrageenan and N-vinyl-2-pyrrolidone.

2. Experimental

2.1. Materials

N-vinyl-2-pyrrolidone (Aldrich) was distilled under reduce pressure at 14 mm Hg and 55 °C and only middle fraction was used. Maleic acid (E. Merck), k-carrageenan (Sigma) and Potassium peroxymonosulphate (Sigma) have been used as such. For maintaining hydrogen ion concentration, sulphuric acid (E. Merck) is 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 used were received from Bokaro steel plant, India.

2.2. Procedure for grafting

All the reactions were carried out in three necked flask under oxygen free nitrogen atmosphere. For each experiment, k-carrageenan (CgOH) solution has been prepared by adding weighed amount of k-carrageenan (CgOH) into the reactor containing triple distilled water with rapid stirring. The calculated amount of N-vinyl-2-pyrrolidone, peroxymonosulphate, maleic acid and sulphuric acid solutions has been added to the reactor at constant temperature and a slow stream of oxygen free nitrogen is passed continuously during the entire course of reaction. A known amount of deoxygenated potassium peroxymonosulphate solution is added to initiate the reaction. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated out by pouring it into water/methanol mixture. The grafted sample has been separated by filtration, dried and weighed. Poly (N-vinyl-2-pyrrolidone) remained in the filtrate. To the filtrate a pinch of hydroquinone has been added and then it is concentrated by distillation under reduced pressure. The concentrated solution is poured into the pure methanol to precipitate poly N-vinyl-2-pyrrolidone. The poly (N-vinyl-2-pyrrolidone) is separated, dried and weighed.

2.3. Study of properties

2.3.1. Swelling test

For the swelling studies, 0.02 g of each grafted sample synthesized by varying the concentration of N-vinyl-2-pyrrolidone, 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).

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

$$S_R = P_S \times 100$$

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 N-vinyl-2-pyrrolidone 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 k-carrageenan and its grafted polymer with N-vinyl-2-pyrrolidone 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 k-carrageenan and k-carrageenan-g-N-vinyl-2-pyrrolidone 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 k-carrageenan and k-carrageenan-g-N-vinyl-2-pyrrolidone has been carried in inert atmosphere at heating rate of 15 °C per minute upto 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.

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

Table 1
Effect of PMS concentration.

[PMS] $\times 10^2$ mol dm^{-3}	%G	%E	%A	%C	%H
0.6	143.3	35.4	58.9	22.7	64.5
1.0	305.6	63.4	75.3	27.0	36.5
1.4	531.1	84.2	84.1	35.4	15.7
1.8	642.1	62.5	86.5	57.7	37.4
2.2	794.0	60.5	88.8	73.7	39.4

[NVP] = 16×10^{-2} mol dm^{-3}, [MEA] = 3.2×10^{-3} mol dm^{-3}, [CgOH] = 1.0 g dm^{-3}, [H$^+$] = 1.5×10^{-3} mol dm^{-3}, Temp. = 40 °C, Time = 120 min.

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

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

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

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

3.2. Determination of optimum reaction conditions

The reaction conditions were optimised by varying the concentration of peroxymonosulphate (PMS), maleic acid (MEA), sulphuric acid, N-vinyl-2-pyrrolidone, k-carrageenan (C_gOH), along with reaction time and temperature and their effect on grafting parameters has been studied.

3.2.1. Effect of peroxymonosulphate concentration

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

3.2.2. Effect of maleic acid concentration

The effect of variation of maleic acid on graft copolymerization has been studied by varying its concentration from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3}. It has been observed that grafting parameters increase on increasing maleic acid concentration up to 3.2×10^{-3} mol dm^{-3} and thereafter grafting ratio, efficiency, add on and conversion decrease where as homopolymer increases The increment in grafting parameters could be explained due to increase in number of primary free radicals (MEA$^\bullet$ and $SO_4^{\bullet -}$), but the concentration of maleic acid beyond 3.2×10^{-3} mol dm^{-3}, these grafting parameters decrease due to the formation of large amount poly (N-vinyl-2-pyrrolidone).

3.2.3. Effect of hydrogen ion concentration

The effect of variation of hydrogen ion concentration on graft copolymerization has been carried out 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, 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 increase. This behaviour might be due to the formation of H_2SO_5 as an inactive species (Pandey, Banerjee, Taunk, & Behari, 2003), thus the concentration of HSO_5^- decreased resulting in less production of primary free radicals, thereby decreasing the grafting parameters. The results are shown in Table 2.

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

3.2.4. Effect of k-carrageenan concentration

The effect of concentration of k-carrageenan on grafting parameters has been studied by varying the concentration of k-carrageenan from 0.6 to 1.4 g dm^{-3}. The table and figures reveals that grafting ratio, add on and efficiency increase on increasing the concentration of k-carrageenan. This increment may be due to availability of more grafting sites, where poly N-vinyl-2-pyrrlidone can be grafted.

3.2.5. Effect of N-vinyl-2-pyrrolidone concentration

The effect of N-vinyl-2-pyrrolidone concentration on graft copolymerization has been studied by varying its concentration from 8×10^{-2} to 24×10^{-2} mol dm^{-3} and the results have been shown in Fig. 1. It has been observed that grafting ratio, add on and efficiency increase on increasing the concentration of N-vinyl-2-pyrrolidone from 8×10^{-2} to 16×10^{-2} mol dm^{-3} . The 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 k-carrageenan macro radicals ($C_gO^\bullet$) 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 decrease might be due to formation of more homopolymer, which increases the viscosity of reaction medium due to which movement of free radicals is hindered.

3.2.6. Effect of time period

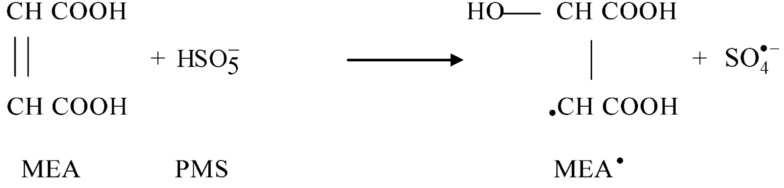
The effect of change in duration of grafting reaction has been studied by varying the time interval from 60 to 180 min. It has been observed that grafting ratio, efficiency and add on increase on increasing the time period from 60 to 120 min. On further increasing the time period, grafting parameters 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 active species, 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 and increment in homopolymer formation.

3.2.7. Effect of temperature

The effect of temperature on grafting parameters has been studied from 30 to 50 °C. It has been observed that as the temperature is increased from 30 to 40 °C, there is an increment 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_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 and resulting in the decrement in the grafting parameters.

3.2.7.1. Mechanism. On the basis of experimental results, the probable reaction mechanism is suggested. Initially peroxymonosulphate interacts with maleic acid to form primary free radicals

$R^\bullet$, which may abstract hydrogen atom from k-carrageenan and thereby producing ($C_gO^\bullet$) macro radicals. The monomer molecules which are in close vicinity of the reaction sites become acceptors of k-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.



$$\mathrm{CH\,COOH{=}CH\,COOH} + HSO_5^- \longrightarrow \mathrm{HO{-}CH\,COOH{-}{}^\bullet CH\,COOH} + SO_4^{\bullet -}$$

MEA PMS MEA$^\bullet$

$R^\bullet$ Represents MEA$^\bullet$ and $SO_4^{\bullet -}$

Initiation:

$$CgOH + R^\bullet \longrightarrow CgO^\bullet + RH$$

$$M + R^\bullet \longrightarrow RM^\bullet$$

Where CgOH = k-carrageenan, M = N-Vinyl-2-pyrrolidone $CgO^\bullet$ (Macro radical)

Propagation:

$$CgO^\bullet + M \longrightarrow CgOM^\bullet$$

$$CgOM^\bullet + M \longrightarrow CgOM_1^\bullet$$

……………………………………

……………………………………

$$CgOM_{n-1}^\bullet + M \longrightarrow CgOM_n^\bullet$$

$$RM^\bullet + M \longrightarrow RM_1^\bullet$$

$$RM_1^\bullet + M \longrightarrow RM_2^\bullet$$

……………………………………

……………………………………

$$RM_{n-1}^\bullet + M \longrightarrow RM_n^\bullet$$

Termination:

$$CgOM_n^\bullet + CgOM_m^\bullet \longrightarrow \text{Graft copolymer}$$

$$RM_n^\bullet + CgOM_n^\bullet \longrightarrow \text{Graft copolymer}$$

$$RM_n^\bullet + RM_m^\bullet \longrightarrow \text{Homopolymer}$$

3.3. *Evidence of grafting*

3.3.1. *IR spectroscopy of k-carrageenan and k-carrageenan-g-N-viny-2-pyrrolidone*

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. Infra red spectrum

Table 2
Effect of $[H]^+$ concentration.

$[H]^+ \times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
0.5	478.8	64.2	82.7	41.8	35.7
1.0	483.6	65.4	82.8	41.5	34.5
1.5	531.1	84.2	84.1	35.4	15.7
2.0	522.9	71.3	83.9	41.2	28.6
2.5	514.9	68.2	83.7	42.4	31.7

[NVP] = 16 × 10^{-2} mol dm^{-3}, [PMS] = 1.4 × 10^{-2} mol dm^{-3}, [MEA] = 3.2 × 10^{-3} mol dm^{-3}, [CgOH] = 1.0 g dm^{-3}, Temp. = 40 °C, Time = 120 min.

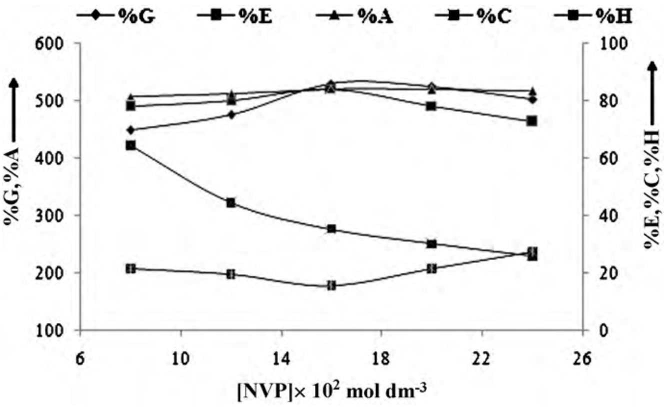


Fig. 1. Effect of concentration of k-carrageenan [NVP] = 16 × 10^{-2} mol dm^{-3}, [PMS] = 1.4 × 10^{-2} mol dm^{-3}, [MEA] = 3.2 × 10^{-3} mol dm^{-3}, [H$^+$] = 1.5 × 10^{-3} mol dm^{-3}, Temp. = 40 °C, Time = 120 min.

of k-carrageenan (Tripathy, Mishra, Yadav, et al., 2009) showed strong peaks at 3504.6 cm^{-1} due to OH stretching vibrations. On comparing the IR spectra of k-carrageenan and k-carrageenan-g-N-viny-2-pyrrolidone, a broad band near at 3504.6 cm^{-1} is due to OH stretching vibration in the spectrum of k-carrageenan. It is observed that there is variation in intensity of OH stretching vibration and shifting of the peak from 3504.6 to 3428.3 cm^{-1} appeared in k-carrageenan-g-N-viny-2-pyrrolidone (Fig. 2) respectively, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band at 1673.1 cm^{-1}due to $\rangle$C=O stretching vibration, and at 1459.2 cm^{-1} due to –CN stretching vibration of monomer molecule respectively. The appearances of additional peaks in spectrum of graft copolymer due to pendant chain of monomer and also shifting of OH out of plane bending vibration at 605.1–627.2 cm^{-1} appeared in the spectrum of k-carrageenan-g-N-vinyl-2-pyrrolidone showed that grafting might have been taken place on OH sites of k-carrageenan.

3.3.2. Thermal analysis of k-carrageenan and k-carrageenan-g-N-viny-2-pyrrolidone

The 10% weight loss has been found at about 106.2 °C which may be due to loss of absorbed water. The degradation of k-carrageenan (Tripathy, Mishra, & Behari, 2009; Tripathy, Mishra, Yadav, et al., 2009) 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 peek present in k-carrageenan DTA curve 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 k-carrageenan has been found to be 253.3 °C. The integral procedural decomposition temperature which accounts the whole shape of the curve and it sum up all of its dips and meanderings in a single number by measuring the area under the curve. Thus thermal stability of pure k-carrageenan and its graft copolymers has also been determined by calculating IPDT values using following equation (Doyle, 1961). The area under the curve divided by the total area is the total curve area, A^*, is normalized with respect to both residual mass and temperature. A^* is converted to a temperature, T_{A^*}, by following equation

$$T_{A*} = (T_{\text{end}} - T_{\text{initial}})A* + T_{\text{initial}} \quad (1)$$

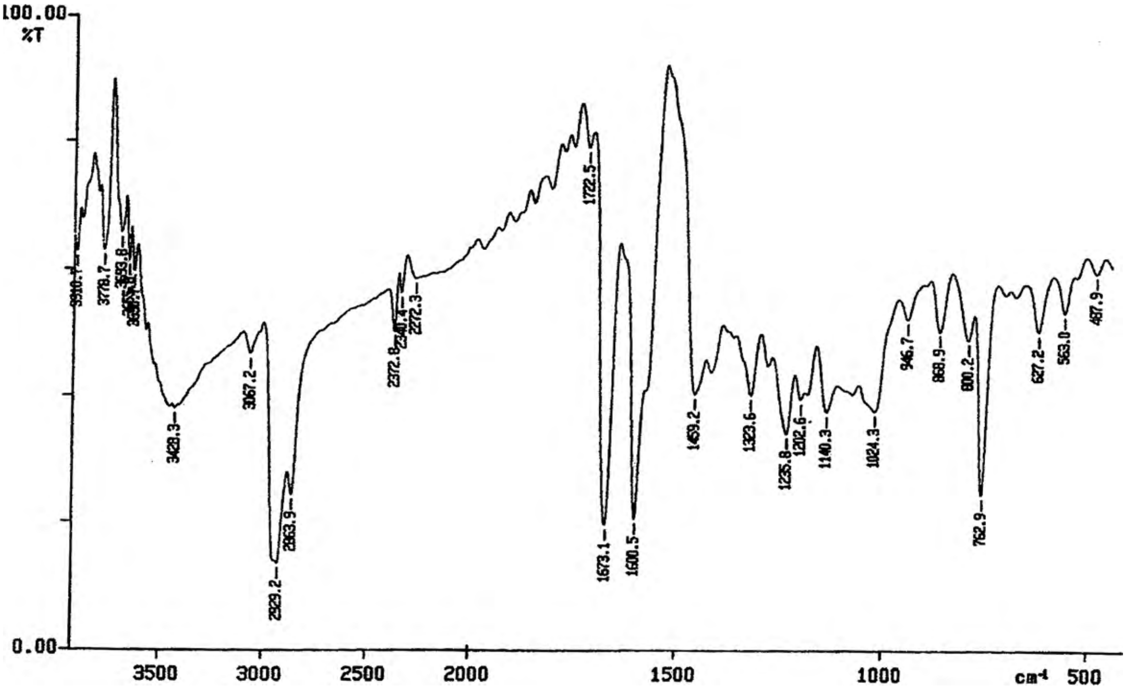


Fig. 2. IR spectrum of k-carrageenan-g-N-viny-2-pyrrolidone.

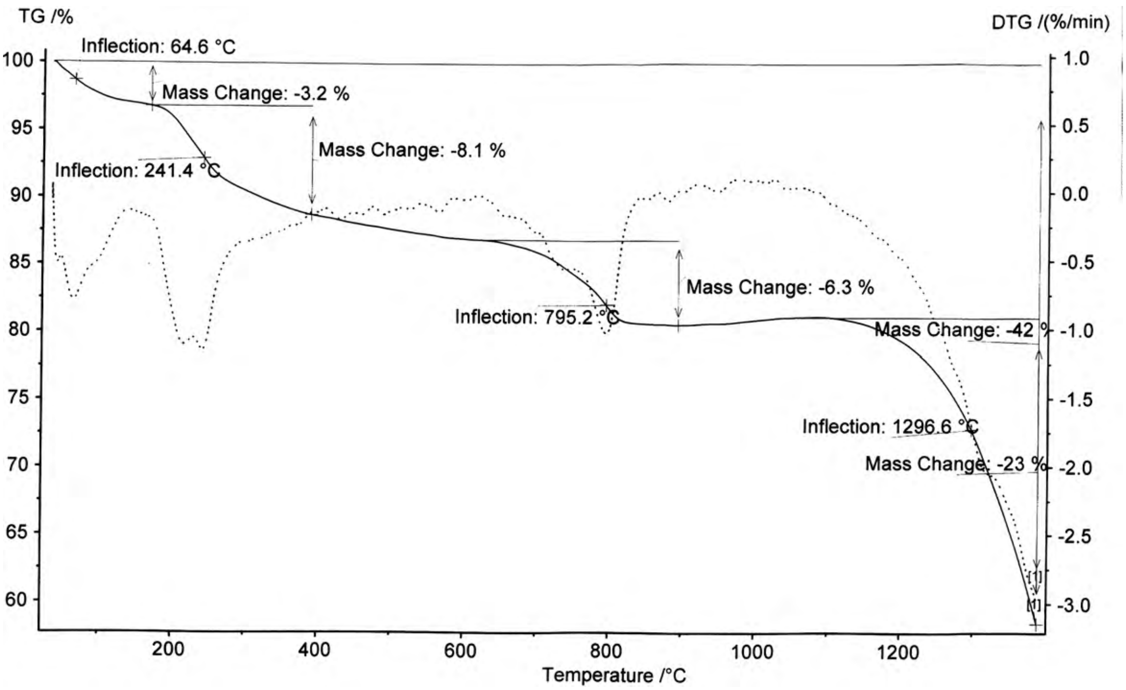


Fig. 3. Thermogravimetric trace of k-carrageenan-g-N-viny-2-pyrrolidone.

T_{A^*} represents a characteristic end of volatilization temperature rather than an IPDT having practical significance. The second curve area K^* can be derived by drawing rectangle bearing X-axis upto T_{A^*} and the Y-axis mass fraction remaining at T_{end}. K^* is the ratio between the area under the curve (inside the rectangle) and total rectangle area. The IPDT determined by substituting A^*K^* for A^* in Eq. (1). The thermogravimetric analysis trace and differential thermal trace of k-carrageenan. But in case of graft copolymer started (Fig. 3) degrading at about 64.6 °C. It is a two steps degradation process. Weight loss of 2.6% up to 100 °C occurred due to loss of absorbed water. Polymer decomposition temperature is found to be 195.5 °C. Only 30% weight loss has been observed at 1318.7 °C. Since the process involves two degradation steps therefore two maximum temperatures ($T_{\max}$) appeared at 241.4 and 795.2 °C. The rate of weight loss increases with increase in temperature from 200 to 800 °C and thereafter attains a maximum at about 1296.6 °C. First $T_{\max}$ at 241.4 °C might be due to elimination of $-OSO_3^-$ from the polymeric backbone, which is also confirmed exothermic peak present in DTA curve of graft copolymer at 283.7 °C. Second $T_{\max}$ at 795.2 °C might be due to elimination of five membered ring from pendent chain attached to the polymeric backbone, which is also confirmed by the exothermic peak present in DTA curve of graft copolymer at 1042.0 °C. The final decomposition temperature and integral decomposition temperature (IPDT) have been found to be at 1318.7 °C and at 658.8 °C respectively. The high value of Polymer decomposition temperature, final decomposition temperature, integral procedural decomposition temperature, and two steps degradation indicate that graft copolymer is more stable than parent polymer backbone.

3.4. Properties

3.4.1. Swelling measurement

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 298% occurs when grafting ratio is 531.1%. Since N-vinyl-2-pyrrolidone is a hydrophilic monomer, it increases the water absorbing capacity and water retention character of graft copolymer. The long pendant chains of N-vinyl-2-pyrrolidone are responsible for maximum hydrophilic character (Nasef, Saidi, Nor, & Foo, 2000) in graft copolymer thereby increasing the value of swelling ratio.

3.4.2. Flocculation performance

At the time of mixing, concentration of flocculants should be very low so that polymer solution is uniformly dispersed. Turbidity values of supernatant liquids have been taken as the measurement of flocculation efficiency of backbone *k*-carrageenan and graft copolymer of N-vinyl-2-pyrrolidone with *k*-carrageenan. Plots of supernatant turbidity versus polymer dosage for coking and non-coking coals are presented in (Fig. 4). It is obvious that grafted copolymer *k*-carrageenan-g-N-vinyl-2-pyrrolidone) shows better performance with low turbidity than *k*-carrageenan itself.

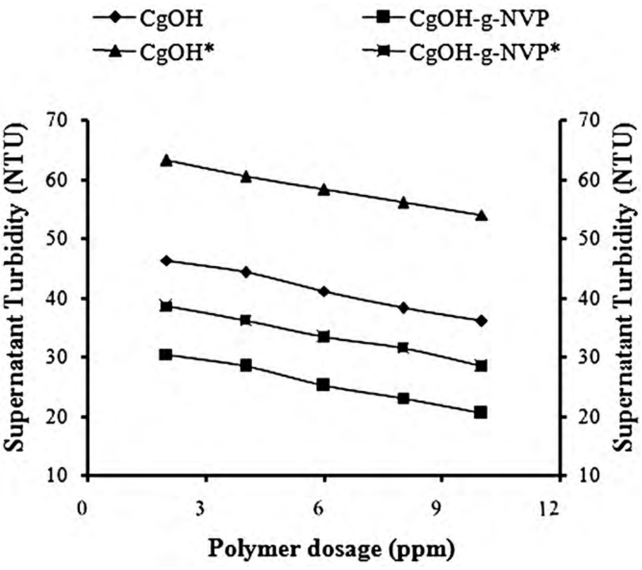


Fig. 4. Effect of polymer dosage on turbidity for coking coal and non-coking coal.

Table 3
Metal ion sorption.

Sample	[NVP] $\times 10^2$ 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	448.4	12.5	4.2	7.5	35.7	11.1	20.4	3.0	1.0	2.0
B	12	475.5	16.6	6.3	22.6	50.0	17.0	73.1	4.0	1.5	6.0
C	16	531.1	22.9	19.1	45.2	74.3	59.2	208	5.5	4.5	12.0
D	20	525.5	20.8	14.8	39.6	65.7	43.7	164	5.0	3.5	10.5
E	24	502.0	18.7	10.6	33.9	57.6	29.7	128	4.5	2.5	9.0

Where CgOH = k-carrageenan, A, B, C, D, E = Graftcopolymers.
[NVP] = 16 × 10^{-2} mol dm^{-3}, [PMS] = 1.4 × 10^{-2} mol dm^{-3}, [CgOH] = 1.0 g dm^{-3}, [MEA] = 3.2 × 10^{-3} mol dm^{-3}, [H^+] = 1.5 × 10^{-3} mol dm^{-3}, Temp. = 40 °C, Time = 120 min.

This phenomenon could be explained by considering bridging mechanism (Deshmukh & Singh, 1987; Gregory, 1982). In grafted copolymer, the dangling of poly (N-vinyl-2-pyrrolidone) chains has better approachability as acrylamide (Bratby, 1980) to the contaminant coal particles hence increasing its flocculation capability (Erciyes, Erim, Hazer, & Yagci, 1992). By grafting of poly (N-vinyl-2-pyrrolidone) onto *k*-carrageenan, efficient flocculant has been obtained and it may be used for the treatment of coal mine waste water.

3.4.3. *Metal ion sorption behavior of k-carrageenan and its graft copolymer*

Hydrophilic–hydrophobic balance and nature of monomer are major factors those effect the metal ion uptake (Lehto, Vaaramaa, Vesterinen, & Tenhu, 1998). These functionalities can be tailored and incorporated by grafting to retain ion by polymer analogous reaction or by simple chelation absorption due to opening of polymer matrix or pores created. Out of these possibilities, all may contribute in the metal ion sorption, though extent of contribution of any factor may be different (Inou, Baba, & Yoshizuka, 1993). However functional group incorporated with the help of grafting by its ability to interact with metal ions may play more important role in determination of selectivity and quantum of metal ion uptake (Sheng, Ting, Chen, & Hong, 2004). Three metal ions have been choosen (Zn^{2+}, $Ni^{2+}$and Pb^{2+}) for the study of metal ions sorption and the amount of metal uptake was calculated by titrating the unabsorbed metal ions (all the solutions were made in triple distilled water). The increment in all these parameters might be due to grafting of N-vinyl-2-pyrrolidone which accounts for the higher sorption of these divalent cations through a chelating reaction (Onsoyen & Skaugrud, 1990) and the results are given in Table 3.

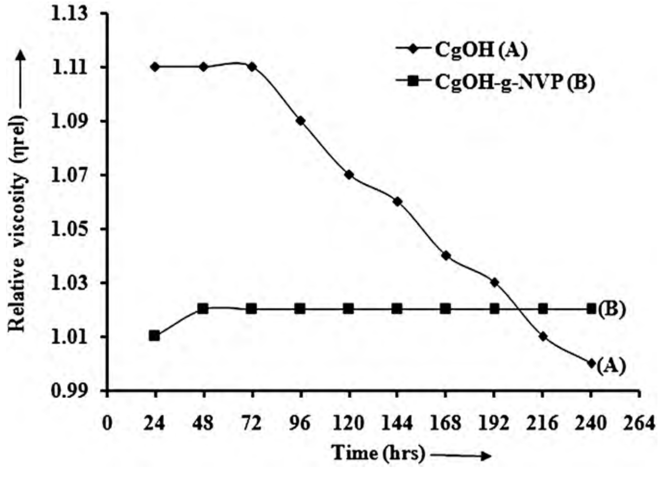


Fig. 5. Relative viscosity vs. time period to study biodegradation of k-carrageenan and graft copolymer.

3.4.4. *Resistance to biodegrabilty*

The results presented in the form of graph in (Fig. 5). From efflux time of polymer solution (t) and that of solvent 1.0 M $NaNO_3$ (t_o), relative viscosity $\eta_{rel} = (\eta/\eta_0)$ was obtained. It has been observed that relative viscosity of k-carrageenan-g-N-vinyl-2-pyrrolidone is lower than k-carrageenan. This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically (Deshmukh, Chaturvedi, & Singh, 1985). k-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. 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 inert poly (k-carrageenan-g-N-vinyl-2-pyrrolidone) 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 (k-carrageenan-g-N-vinyl-2-pyrrolidone) graft onto k-carrageenan through graft copolymerization, the drag reduction effectiveness can be enhanced and biodegradation can be minimized.

4. Conclusion

A graft copolymer of k-carrageenan and N-vinyl-2-pyrrolidone has been synthesized by using efficient redox pair, i.e. PMS/maleic acid. The spectroscopic data confirm that the grafting of N-vinyl-2-pyrrolidone has taken place at hydroxyl group of k-carrageenan. The thermogravimetric analysis data shows that the k-carrageenan-g-N-vinyl-2-pyrrolidone is thermally more stable than the k-carrageenan. The synthesized graft copolymer shows good swellability to wards water. The synthesized graft copolymer, i.e. k-carrageenan-g-N-vinyl-2-pyrrolidone shows better swelling, metal ion sorption and flocculating properties.

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