

Modification of κ -Carrageenan by Graft Copolymerization of Methacrylic Acid: Synthesis and Applications

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ABSTRACT: In this article, the synthesis of κ -carrageenan-g-methacrylic acid has been reported by free radical polymerization initiated by Potassium peroxymonosulphate/glycolic acid redox pair under nitrogen atmosphere. The reaction conditions have been optimized by varying the reaction conditions, including the concentration of monomer, peroxymonosulphate, glycolic acid, sulphuric acid, κ -carrageenan along with reaction time and temperature. It has been observed that the maximum yield has been obtained at time 120 min, temperature 40°C, at 20×10^{-2} mol dm⁻³ concentration of methacrylic acid, 1.0 g dm⁻³ concentration of κ -carrageenan and 16×10^{-3} mol dm⁻³ concentration of per-

oxymonosulphate. The graft copolymer is characterized by Fourier Transform Infrared Spectroscopy and Thermal analysis. Water swelling capacity of graft copolymer has been determined. Intrinsic viscosity has been obtained for both grafted and ungrafted κ -carrageenan. Metal ion sorption and flocculation performance of synthesized graft copolymer has been studied with respect to the ungrafted substrate. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3896–3905, 2009

Key words: κ -carrageenan; graft copolymer; thermal analysis; methacrylic acid; metal ion uptake; water swelling behavior and flocculation

INTRODUCTION

In this era, much emphasis has been given for modification of natural polymers, through vinyl graft copolymerization onto polysaccharide backbones, which is a quite relied and well-known method for the synthesis of biopolymer-based advanced materials.^{1–4} 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.^{5,6} κ -Carrageenan are sulfated anionic polygalactans extracted from marine red algae^{7,8} (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-sulfate and (1→4)- β -3,6-anhydro-D-galactose residues.^{9–11} Carrageenans and their derivatives form valuable ingre-

dients for foods, cosmetics, and pharmaceuticals.^{12,13} Carrageenan oligomers have been reported to have anti-HIV (Human Immuno deficiency Virus) activities.^{14,15} In recent years, they have been demonstrated to play significant role in antioxidant activities^{16–18} and explored as effective excipients in controlled-release drug delivery systems.^{19–21} However, κ -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 κ -carrageenan are scantily available^{22,23} 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 methacrylic acid using peroxymonosulphate/glycolic acid redox pair. The optimum grafting conditions have been obtained, and studies have been carried on swelling capacity, metal ion sorption, and flocculating ability.

EXPERIMENTALS

Materials

Methacrylic acid (Sigma Aldrich Co. Ltd, Gillingham, Dorset, SP8 4XT, UK) was distilled in the presence of copper turnings under reduced pressure

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(14 mm and 55°C), and only middle fraction was used. Potassium peroxydisulphate (Sigma, USA.) and glycolic acid (GA) (E. Merck, India) have been used as such without further purification. κ -Carrageenan was purchased from (Sigma Aldrich, UK). For maintaining hydrogen ion concentration, sulphuric acid (E. Merck, India) was used. The other chemical reagents were of analytical grade. All the solutions were prepared in triple distilled water. For flocculation studies, coking and noncoking coals used were received from steel Plant, Bokaro, India.

Procedure for grafting

All the reactions have been carried out in nitrogen atmosphere. 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 methacrylic acid, glycolic acid, and sulphuric acid solutions were added in the reactor, and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium peroxydisulphate 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 methanol–water mixture. The precipitate was separated, dried, and weighed. The poly(methacrylic acid) remained in the filtrate. To the filtrate a pinch of hydroquinone was added and concentrated by distillation under reduce pressure. The poly(methacrylic acid) was precipitated by acidifying the solution (5N H₂SO₄). The poly (methacrylic acid) thus obtained was separated, dried, and weighed.

Characterization

FTIR 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, Chennai, India in the range 500– 4000 cm⁻¹.

TGA analysis

The thermal analysis of κ -carrageenan and methacrylic acid 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, Chennai, India.

Swelling test

Swelling studies have been carried out with different grafted samples synthesized by varying the concentration of methacrylic acid. 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.²⁴

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 methacrylic acid from 12 to 28 × 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 behavior of κ -carrageenan, and its grafted polymer with methacrylic acid has been determined in terms of different parameters,²⁵ i.e., percent ion uptake (Pu), partition coefficient (Kd), retention capacity (Qr).

Determination of viscosity of polymer solution

During the measurement, temperature was maintained at 30°C ± 0.1°C in thermostat. From efflux time of polymer solution (t) and that of solvent i.e., 1.0 M NaCl (t_0), relative viscosity $\eta_{rel} = \eta / \eta_0$ was obtained. Specific viscosity was calculated from the relationship $\eta_{sp} = \eta_{rel} - 1$. Reduced viscosity for a set of five polymer solutions is calculated having concentrations in (g/dL). Intrinsic viscosity was then obtained from common ordinate intercept on extrapolation of plots of reduced viscosity versus concentration.

Flocculation test

In 1 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, Varanasi, India) to express the turbidity in nephelometric unit (NTU).

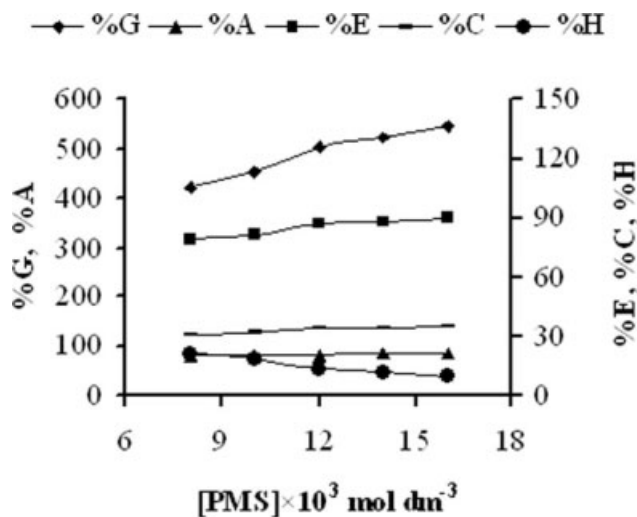


Figure 1 Effect of peroxymonosulphate concentration $[C_{A}OH] = 1.0 \text{ g dm}^{-3}$, $[Glycolic \text{ acid}] = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$, $[MAA] = 20 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^{+}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. = 40°C , Time = 120 min. %G = Grafting ratio; %A = Add on; %C = Conversion, %E = Efficiency, %H = Homopolymer.

RESULT AND DISCUSSION

The graft copolymer has been characterized as reported in the literature.²⁶

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

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

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

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

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

Determination of optimum reaction conditions

The effect of variation in concentration of peroxymonosulphate (PMS), glycolic acid (GA), sulphuric acid, methacrylic acid (MAA), κ -carrageenan ($C_{A}OH$), reaction time, and temperature on grafting parameters has been studied.

Effect of peroxymonosulphate concentration

The effect of potassium peroxymonosulphate on grafting parameters has been studied by varying the concentration of peroxymonosulphate. It has been found that the grafting ratio, add on, efficiency and conversion increase on increasing the concentration of peroxymonosulphate (PMS) throughout the cited

range i.e., from 0.8 to $1.6 \times 10^{-3} \text{ mol dm}^{-3}$ (Fig. 1). This behavior might be attributed due to progressive reduction of peroxymonosulphate by glycolic acid producing primary free radicals,²⁷ which attack on the κ -carrageenan molecules creating more active sites to which monomer addition takes place.

Effect of glycolic acid concentration

The effect of variation of glycolic acid on graft copolymerization has been studied by varying its concentration from 1.6 to $4.8 \times 10^{-3} \text{ mol dm}^{-3}$, and results are being summarized in Table I. It has been observed that grafting parameters increase on increasing glycolic acid concentration up to $3.2 \times 10^{-3} \text{ mol dm}^{-3}$ and after that add on, grafting ratio, efficiency, and conversion decrease, whereas homopolymer increases. This could be explained due to increase in number of primary free radicals (GA° and OH); however, in high concentration of glycolic acid i.e., beyond $3.2 \times 10^{-3} \text{ mol dm}^{-3}$, formation of more poly(methacrylic acid) takes place, which decreases grafting efficiency and increases homopolymer percentage.

Effect of methacrylic acid concentration

The effect of methacrylic acid (MAA) concentration on graft copolymerization has been studied by varying its concentration from 12.0 to $28.0 \times 10^{-2} \text{ mol dm}^{-3}$, and results have been presented in form of Figure 2. It has been observed that grafting parameters increase on increasing the concentration of methacrylic acid (MAA) from $12.0 \times 10^{-2} \text{ mol dm}^{-3}$ to $20.0 \times 10^{-2} \text{ mol dm}^{-3}$, and this increment can 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 ($C_{A}O^{\bullet}$) resulting in chain initiation and thereafter themselves becomes free radical donors to neighboring molecules leading to lowering of termination. But beyond $20.0 \times 10^{-2} \text{ mol dm}^{-3}$, grafting parameters decrease

TABLE I
Effect of Glycolic Acid Concentration

$[GA] \times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
1.6	445	81.3	81.6	31.8	18.7
2.4	481	83.2	82.8	33.5	16.8
3.2	503	86.8	83.1	33.6	13.1
4.0	470	82.6	82.4	33.0	17.3
4.8	422	79.0	80.8	30.9	21.0

$[MAA] = 20 \times 10^{-2} \text{ mol dm}^{-3}$, $[PMS] = 12 \times 10^{-3} \text{ mol dm}^{-3}$, $[C_{A}OH] = 1.0 \text{ g dm}^{-3}$, $[H^{+}] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. = 40°C , Time = 120 min.

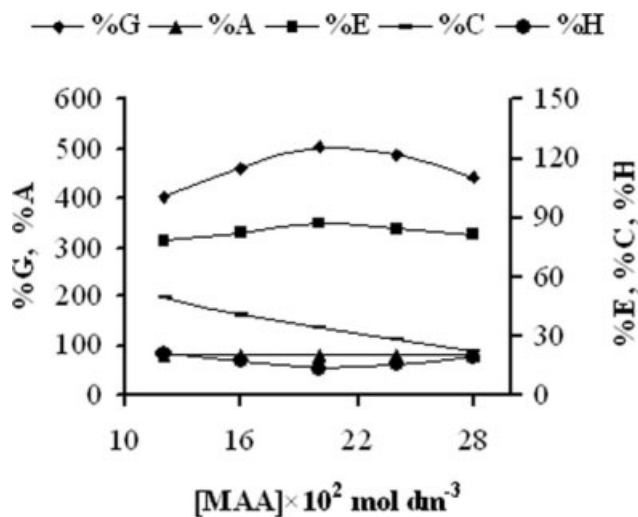


Figure 2 Effect of methacrylic acid concentration $[C_AOH] = 1.0 \text{ g dm}^{-3}$, $[Glycolic \text{ acid}] = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$, $[PMS] = 12 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. = 40°C , Time = 120 min, %G = Grafting ratio; %A = Add on; %C = Conversion, %E = Efficiency, %H = Homopolymer.

which might be attributed to increased viscosity of reaction medium due to formation of more homopolymer.

Effect of hydrogen ion concentration

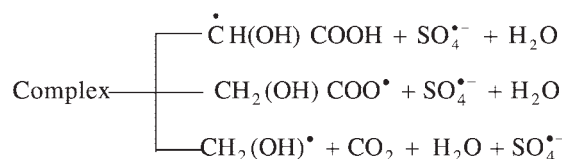
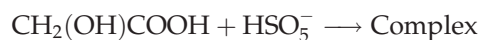
To examine the effect of hydrogen ion concentration on graft copolymerization, the reaction has been carried at various concentration of sulphuric acid i.e., from $2 \times 10^{-3} \text{ mol dm}^{-3}$ to $10 \times 10^{-3} \text{ mol dm}^{-3}$, and results are shown in Table II. The grafting parameters increase continuously on increasing the concentration of hydrogen ion upto $6 \times 10^{-3} \text{ mol dm}^{-3}$; however, beyond that grafting parameters decrease, whereas homopolymer increases. This could be explained due to the fact that in aqueous medium glycolic acid ionizes and in presence of

TABLE II
Effect of $[H^+]$ Concentration

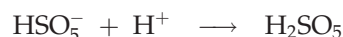
$[H^+] \times 10^3$ mol dm ⁻³	%G	%E	%A	%C	%H
2	400	78.0	80.0	29.8	20.0
4	466	82.3	82.3	32.9	17.6
6	503	86.8	83.1	33.6	16.8
8	442	81.5	81.5	31.4	18.5
10	396	77.1	79.8	29.8	20.2

$[MAA] = 20 \times 10^{-2} \text{ mol dm}^{-3}$, $[PMS] = 12 \times 10^{-3} \text{ mol dm}^{-3}$, $[GA] = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$, $[C_AOH] = 1.0 \text{ g dm}^{-3}$, Temp. = 40°C , Time = 120 min.

acid concentration $\text{CH}_2(\text{OH})\text{COO}^-$ reacts with H^+ giving more undissociated glycolic acid, which when reacts with PMS forms a complex and gives primary free radical resulting in increase in the value of these parameters.



But on further increasing the hydrogen concentration, H^+ react with HSO_5^- forming inactive H_2SO_5 species, which thereby reducing HSO_5^- concentration results into less production of primary free radicals, which govern graft copolymerization.



Effect of κ -carrageenan concentration

The grafting of methacrylic acid onto κ -carrageenan has been studied at different concentrations of κ -carrageenan. As the concentration of κ -carrageenan increased from 0.4 to 1.0 g dm^{-3} (Fig. 3), the grafting ratio, add on, conversion have been found to increase. This may be due to availability of more grafting sites with increasing concentration of κ -

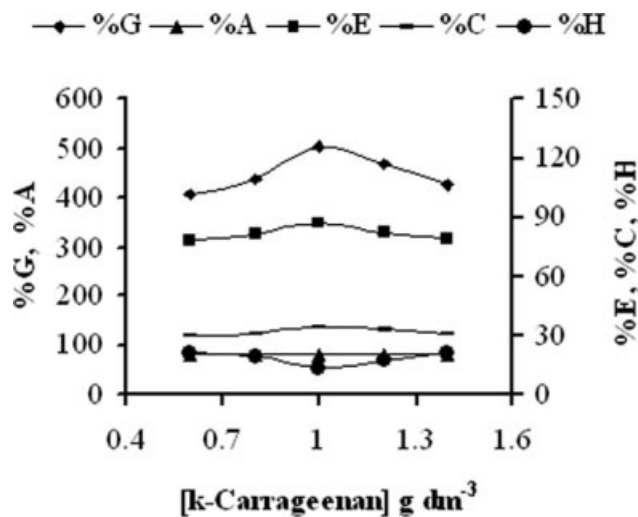


Figure 3 Effect of κ -carrageenan $[PMS] = 12 \times 10^{-3} \text{ mol dm}^{-3}$, $[MAA] = 20 \times 10^{-2} \text{ mol dm}^{-3}$, $[H^+] = 6 \times 10^{-3} \text{ mol dm}^{-3}$, $[Glycolic \text{ acid}] = 3.2 \times 10^{-3} \text{ mol dm}^{-3}$, Temp. = 40°C , Time = 120 min. %G = Grafting ratio, %A = Add on; %C = Conversion, %E = Efficiency, %H = Homopolymer.

carrageenan. As the concentration of κ -carrageenan further increased beyond 1.0 g dm^{-3} , viscosity of reaction medium increases, which hinders the movement of free radicals thereby, decreases the grafting parameters.

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 increased from 30 to 45°C , there was an increase in value of grafting parameters. The increment in grafting parameters upto 45°C is due to the fact that with increase in temperature, rate of production of primary free radicals increase, resulting in propagation of growing grafted chain however, beyond 45°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.

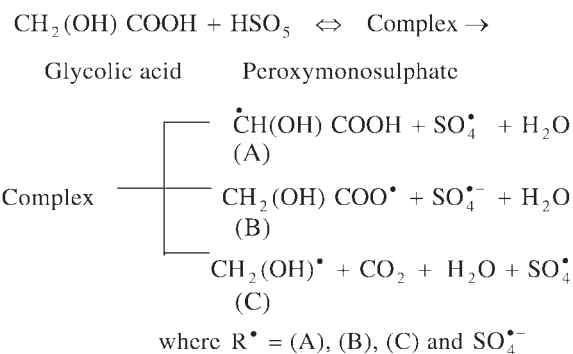
Effect of time

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 reaction duration from 60 to 120 min. On further increment in time, grafting parameters show decreasing trend. This behavior may be explained due to the fact that on increasing the reaction time, propagation of grafting chains takes place due to availability of more active species, which accounts for higher grafting. On further increase in time interval, the mutual annihilation of growing grafted chain occurs, which results in decrement of grafting parameters and increment in homopolymer formation.

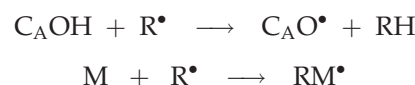
Mechanism

On the basis of experimental results, the probable reaction mechanism is suggested. Initially peroxymonosulphate interacts with glycolic acid to form complex. Subsequently the complex decomposes to generate free radicals R^\bullet , which may abstract hydrogen atom from κ -carrageenan molecule and thereby producing κ -carrageenan ($\text{C}_A\text{O}^\bullet$) macroradicals. The methacrylic acid molecules, which are in close vicinity of the reaction sites, become acceptors of κ -carrageenan radical resulting in chain initiation of graft copolymer and thereafter themselves become free radical donors to neighboring molecules. In this way, grafted chains grow and terminate by coupling

of lone electron at each end of the growing grafted chains to give graft copolymer.

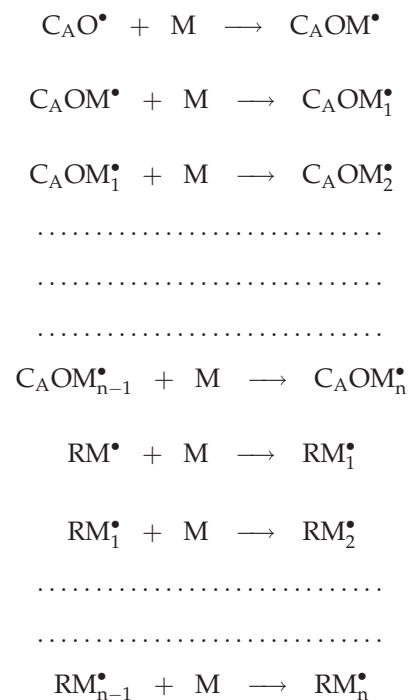


Initiation

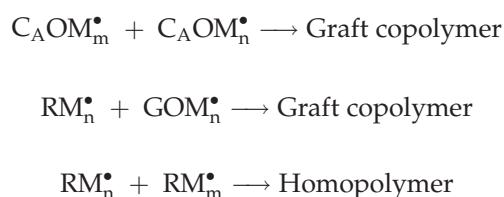


where $\text{CAOH} = k$ -Carrageenan; $\text{M} = \text{Monomer}$

Propagation



Termination



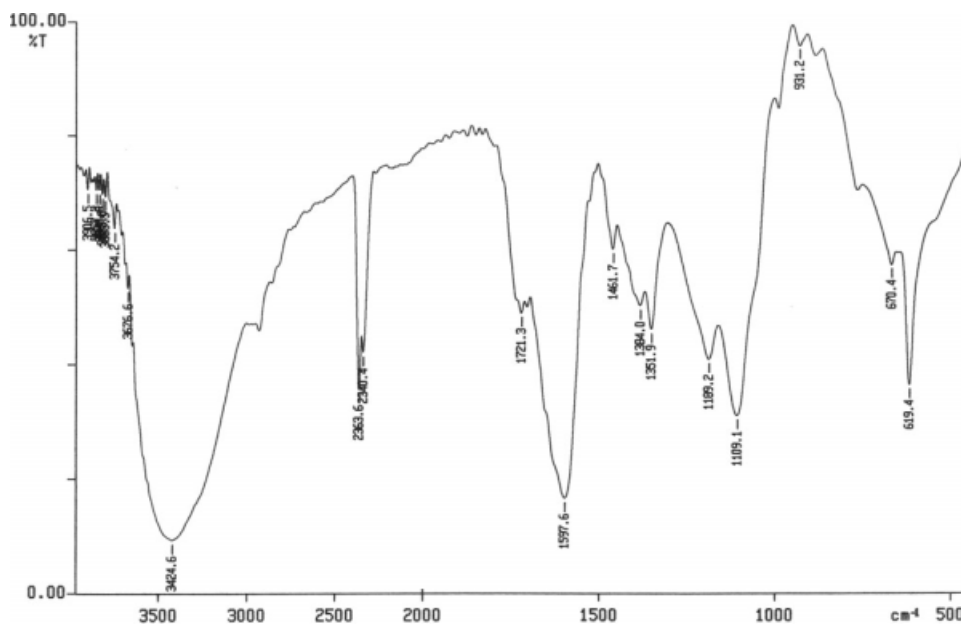


Figure 4 IR spectrum of κ -carrageenan-g-methacrylic acid.

Evidence of grafting

FTIR analysis of spectra of κ -carrageenan and grafted κ -carrageenan-g-methacrylic acid

On comparing the IR spectra of κ -carrageenan²⁸ and κ -carrageenan-g-methacrylic acid (Fig. 4), some additional peaks have appeared in the spectrum of κ -carrageenan-g-methacrylic acid. In comparison to κ -carrageenan, κ -carrageenan-g-methacrylic acid spectrum shows a variation of intensity of $-\text{OH}$ stretching vibration indicating the participation of group in chemical reaction. In addition to this, the grafting of monomer is confirmed by characteristic absorption bands at 1721 cm^{-1} and 1461 cm^{-1} due to $\text{C}=\text{O}$ stretching and OH bending

vibration of carboxylic acid group of monomer. The band at 1109 cm^{-1} provides proof for the formation of ether linkage of polysaccharide backbone with monomer. The presence of additional bands and disappearances of OH stretching vibrations and OH bending vibrations from the spectrum of κ -carrageenan-g-methacrylic acid shows that grafting might have taken place on OH sites of backbone.

Thermogravimetric analysis

κ -carrageenan. The thermal analysis of κ -carrageenan²⁸ shows a weight loss of 8% at about 105°C

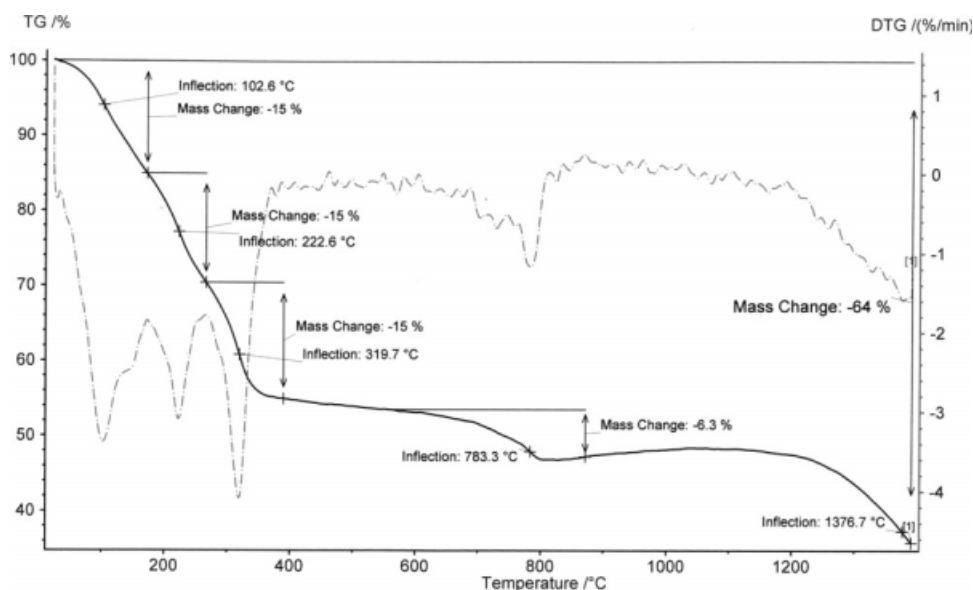
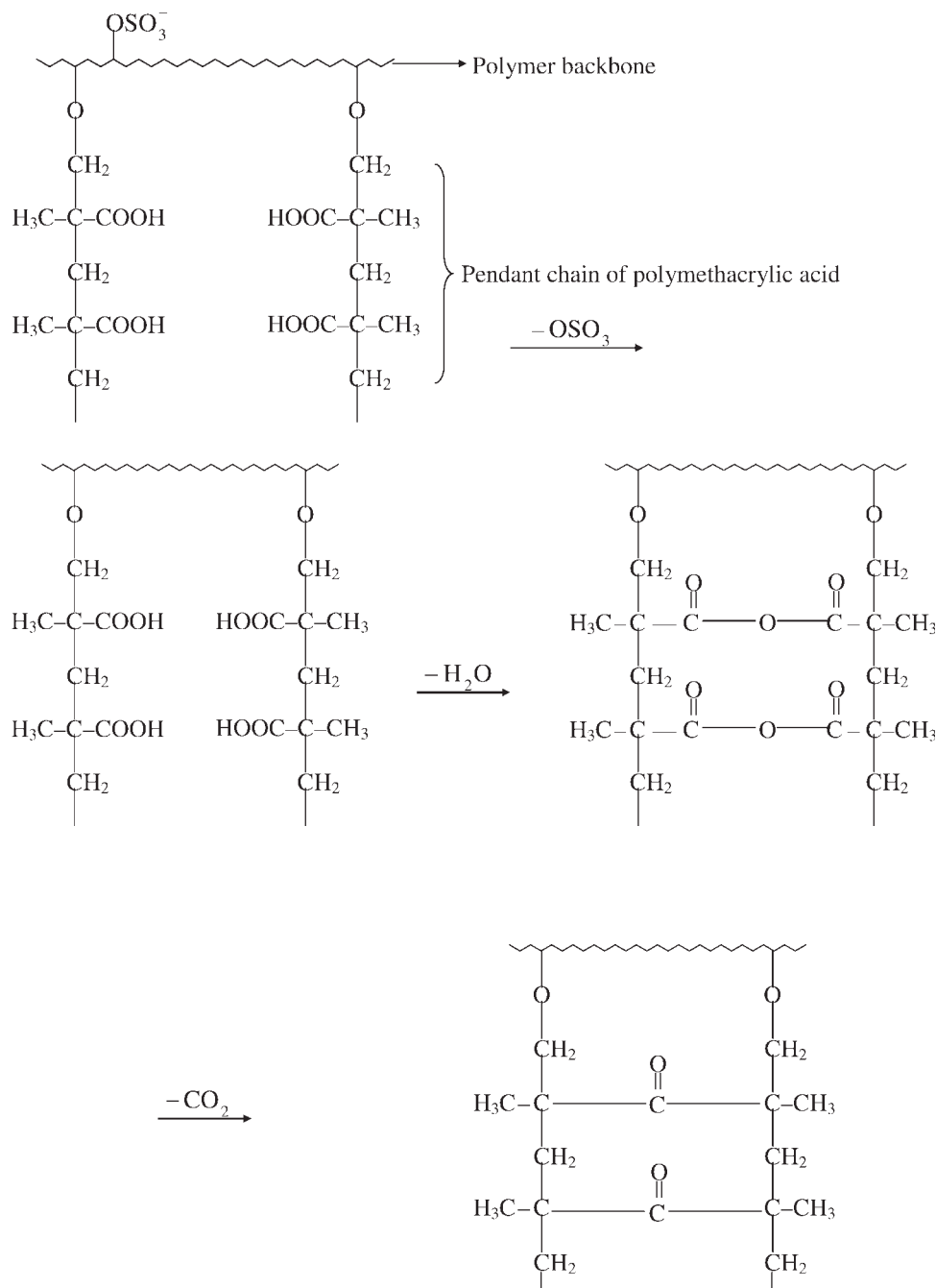


Figure 5 Thermogravimetric Trace of κ -carrageenan-g-methacrylic acid.



Scheme 1 Schematical presentation of degradation pathway of graft polymer.

due to loss of absorbed and bound water. The degradation of κ -carrageenan has started at about 140°C . The degradation has taken place in only single step. The rate of weight loss increased gradually after 200°C with a weight loss of 60% up to 700°C . The polymer decomposition temperature (PDT) and temperature at which maximum degradation takes place i.e. T_{max} have been found at 150°C and 212°C respectively. Integral procedural temperature (IPDT) of carrageenan has been found to be 253°C . Final decomposition temperature is observed at 762°C ,

and about 23% char yield has been obtained at 900°C .

κ -carrageenan-g-methacrylic acid. In the thermogravimetric analysis curve of $\text{C}_A\text{OH-g-MAA}$ (Fig. 5), a weight loss of 6% is observed at 100°C , which is due to loss of absorbed and bound water. The degradation appears to be three stage processes i.e. from 140 to 225°C , from 250 to 360°C and attained a constant rate up to 690°C and thereafter degraded rapidly up to 820°C with a weight loss of 52% up to 800°C . Therefore, three are observed at 219, 313, and

TABLE III
Swelling Test

Sample	[MAA] × 10 ² mol dm ⁻³	%G	Swelling ratio (Sr)	Percent swelling (Ps)
A	12	402	1.7	170
B	16	462	2.6	260
C	20	503	3.5	350
D	24	486	2.9	290
E	28	442	2.1	210

[MAA] = 20 × 10⁻² mol dm⁻³, [PMS] = 12 × 10⁻³ mol dm⁻³, [C_AOH] = 1.0 g dm⁻³, [H⁺] = 6 × 10⁻³ mol dm⁻³, Temp. = 40°C, Time = 120 min Where A, B, C, D and E = Graft copolymer.

760°C, respectively. The polymer decomposition temperature is found to be at 162°C i.e., higher than that of ungrafted κ-carrageenan and final decomposition temperature (FDT) of κ-carrageenan-g-methacrylic acid is found at 832°C, which is also higher than that of κ-carrageenan. The integral procedural temperature is found to be at 306°C and a char yield of 47% is obtained at 900°C. The high value of FDT, IPDT, and char yield indicates that the graft copolymer is more thermally stable than the ungrafted κ-carrageenan. The schematic degradation steps are presented as Scheme 1.

Swelling capacity

The results of swelling studies reveal that swelling of graft copolymer is dependent upon percent grafting ratio. Since the increment in percent grafting is directly related with monomer concentration, thus water retention capacity and hydrophilicity are increased with increase in concentration of hydrophilic monomer i.e., methacrylic acid. It has been observed that a maximum percent swelling of 350% is obtained when grafting ratio is 503%. With the increase in percent grafting, length of pendent of poly (methacrylic acid) increases, which helps in holding more water, thereby increasing the swelling capacity of graft copolymer (Table- III).

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

The result of sorption behavior of κ-carrageenan and its grafted polymer with methacrylic acid has been determined in terms of percent ion uptake (Pu), partition coefficient (Kd), retention capacity (Qr). The results are summarized in (Table- IV), which depicts that the values of percent ion uptake (Pu), partition coefficient (Kd), and retention capacity (Qr) increase directly as percent grafting increases, which might be due to the fact that as grafting increases, pendent chain of poly (methacrylic acid) increases, which offers additional sites for metal ion sorption. Thus, with the incorporation of more functional groups of polymethacrylic acid, number of sorption sites increase, thereby enhancing the sorption capacity of grafted κ-carrageenan as compared with the ungrafted carrageenan. The order of selectivity of sorption of metal ions is Cu⁺⁺ > Ni⁺⁺ > Zn⁺⁺ > Pb⁺⁺ > Hg⁺⁺.

Viscosity of polymer solutions

Intrinsic viscosity was obtained from common ordinate intercept on extrapolation of plots of reduced viscosity versus concentration shown in (Fig. 6). It has been found that intrinsic viscosity value for κ-carrageenan-g-methacrylic acid is lower than κ-carrageenan, which may be attributed due to availability of longer grafted chains, which makes the polymeric chain flexible and thus reduces the viscosity drastically.²⁹

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 κ-carrageenan and graft copolymer of methacrylic acid

TABLE IV
Metal Ion Sorption Test

Sample	[MAA] × 10 ² mol dm ⁻³	%G	Percent uptake (Pu)					Partition coefficient (Kd)					Retention capacity (Qr)				
			Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺	Cu ²⁺	Pb ²⁺	Ni ²⁺	Zn ²⁺	Hg ²⁺
C _A OH	—	—	4.8	2.6	4.5	3.2	1.1	25.3	13.2	23.4	16.3	5.4	2.3	1.3	2.2	1.6	0.5
A	12	402	6.3	3.6	5.9	4.8	1.7	33.5	18.4	31.7	24.8	8.6	3.0	1.8	2.9	2.4	0.8
B	16	462	7.5	5.3	7.1	6.5	3.8	40.8	28.2	38.5	34.8	19.8	3.6	2.7	3.4	3.3	1.8
C	20	503	9.2	6.7	8.6	7.1	5.9	53.7	36.1	47.2	38.2	31.6	4.4	3.4	4.2	3.6	2.8
D	24	486	7.9	6.1	7.7	6.7	4.9	43.3	32.6	42.2	35.9	25.7	3.8	3.1	3.8	3.4	2.3
E	28	442	6.9	4.7	6.5	5.5	3.4	37.2	24.9	35	29.2	17.6	3.3	2.4	3.2	2.8	1.6

[MAA] = 20 × 10⁻² mol dm⁻³, [PMS] = 12 × 10⁻³ mol dm⁻³, [C_AOH] = 1.0 g dm⁻³, [H⁺] = 6 × 10⁻³ mol dm⁻³, Temp. = 40°C, Time = 120 min Where C_AOH= κ-carrageenan A, B, C, D, and E are graft copolymers (κ-carrageenan-g-methacrylic acid).

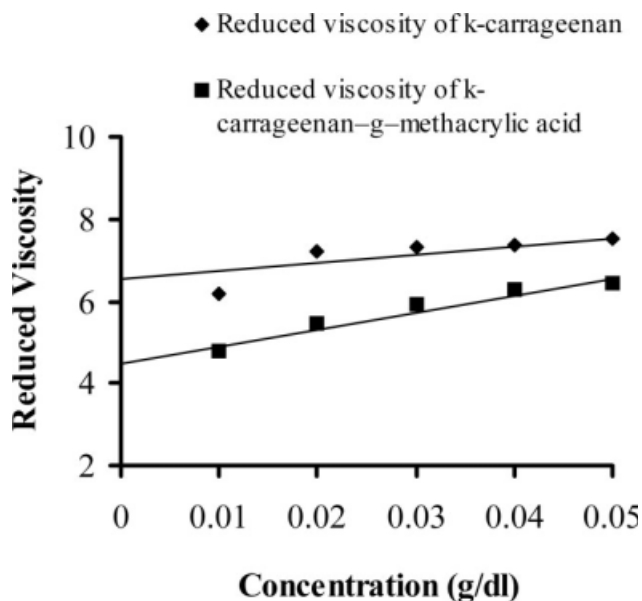


Figure 6 Determination of intrinsic viscosity $[\eta] = 6.5$ of κ -carrageenan and $[\eta] = 4.4$ of κ -carrageenan-g-methacrylic acid.

with κ -carrageenan. Plots of supernatant turbidity versus polymer dosage for coking and noncoking coals are given in (Fig. 7). It has been found that grafted copolymer (κ -carrageenan-g-methacrylic acid) shows better performance than κ -carrageenan itself which could be explained due to the fact that in grafted copolymer, the dangling of poly (methacrylic acid) chains have better approachability to the contaminant coal particles.³⁰ Here the bridging mechanism operates,³¹ which involves binding or bridging individual particles to form flocs, hence increases its flocculation capability.³² By grafting of

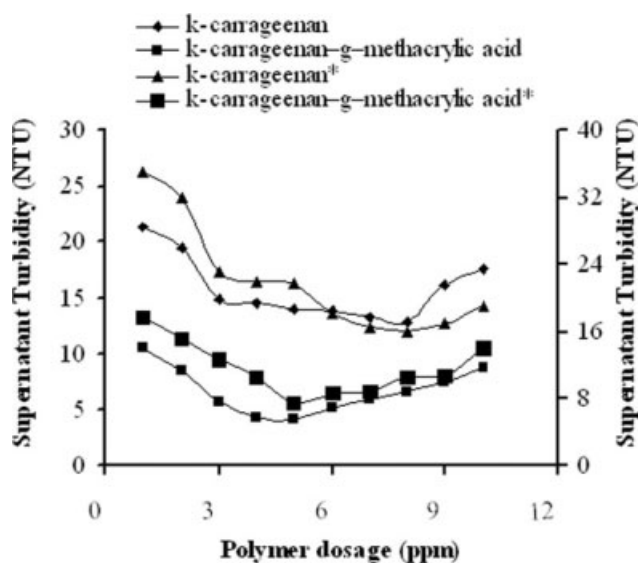


Figure 7 Effect of polymer dosage on turbidity for coking and noncoking coal*.

poly methacrylic acid onto κ -carrageenan, efficient flocculants have been obtained.

CONCLUSIONS

The spectroscopic data confirm that the grafting of methacrylic acid has occurred at hydroxyl group, and it also confirms the mechanism suggested for grafting. 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 with substrate. Grafted polymer shows very good water swelling ability. Grafting is further supported by enhanced properties like metal ion uptake and flocculation efficiency.

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