Synthesis and Characterization of Alginate-*g*-vinyl Sulfonic Acid with a Potassium Peroxydiphosphate/Thiourea System

Arpit Sand, Mithilesh Yadav, Kunj Behari

Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad, India

ABSTRACT: Alginate-*g*-vinyl sulfonic acid graft copolymer was synthesized through the graft copolymerization of vinyl sulfonic acid (VSA) onto alginate with an efficient system, i.e., potassium peroxydiphosphate (PDP)/thiourea in an aqueous medium. The effects of the concentration of thiourea, PDP, hydrogen ion, alginate, and VSA along with the time and temperature on the graft copolymerization were studied by the determination of the grafting parameters (grafting ratio, add-on, conversion, grafting efficiency, and homopolymer). The synthesized graft copolymer was characterized by FTIR analysis. Thermogravimetric analysis showed that the alginate-*g*-vinyl sulfonic acid is thermally more stable than alginate. Water swelling capacity, metal ion sorption, flocculation, and resistance to biodegradability studies of synthesized graft copolymer have been performed with respect to the parent polymer. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 3685–3694, 2010

Key words: graft copolymer; alginate; vinyl sulfonic acid; potassium peroxydiphosphate; thiourea

INTRODUCTION

Considerable interests have shown on chemical modification of natural polymers for imparting desirable properties onto them. In recent years, chemical modification of natural polymers through grafting,[1–3] has received wide spread attention and has paramount contribution toward their improved industrial applications. In our laboratory, by the process of grafting, physical and chemical properties of synthetic monomer are superimposed onto the properties of different natural polymers using redox system.[4,5] In the present study, an attempt has been made not only to increase the paramount contribution toward their industrial applications but also to enhance the properties of such new type of natural polysaccharide as alginate among various natural polysaccharides, which is widely, used water soluble polysaccharide. Alginate, also called algin or alginic acid, is a naturally occurring colloidal hydrophilic polysaccharide obtained from the various species of brown seaweed (phaceophyceae).[6,7] It is a linear copolymer consisting mainly residue of β-1,4-linked D-mannuronic acid and α-1, 4-linked L-glucuronic acid.[8–10] It has a broad range of applications in pharmaceutical,[11,12] biomedical,[13] and agricultural areas.[14,15] It also plays an important role as an adduct product[16] to food due to its property forming highly viscous solution. Some workers reported that alginate is easily capable to form a gel[17,18] in the presence of divalent cation as the calcium ion.

Poly(vinyl sulfonic acid, sodium salt) (PVSA) has negatively chargeable sulfonate groups and is a blood compatible material. Many researchers have reported that the incorporation of sulfonate groups into substrates reduces protein adsorption or platelet adhesion, due to the negatively charged character of these groups, in aqueous solutions.[19] Lee and Oh reported that negatively chargeable sulfonate groups may be a very good candidate for a coating material for improved blood compatibility.

Prompted by the applications of vinyl sulfonic acid and alginate, hitherto unreported graft copolymer viz. graft copolymer (alginate-*g*-vinyl sulfonic acid) has been prepared by employing potassium peroxydiphosphate/thiourea redox system and some of the properties water swelling capacity, metal ion sorption, flocculation, and resistance to biodegradability studies has been investigated.

EXPERIMENTAL

Materials

Vinyl sulfonic acid (VSA) (Aldrich, USA) has been purified by removing the inhibitor by partition method employing diethyl ether as a solvent. Alginate was purchased from Sigma, USA and Thiourea (Merck, India) was used as received. Potassium peroxydiphosphate was received as a gift sample from

FMC (United States), was used as such. For maintaining hydrogen ion concentration sulphuric acid (E. Merck, India) was used and all the solutions were prepared in triple distilled water. The other chemicals used were of analytical grade and used as such without further purification.

Procedure for graft copolymerization

For each experiment alginate solution has been prepared by addition of weighed amount of alginate into reactor containing triple distilled water with rapid stirring. The calculated amount of vinyl sulfonic acid, potassium peroxydiphosphate, thiourea, and sulphuric acid solutions have been added to the reactor at constant temperature and a slow stream of oxygen free nitrogen is passed. After 30 min, a known amount of deoxygenated potassium peroxydiphosphate, solution is added to initiate the reaction, and reaction has been carried under oxygen free nitrogen gas. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring it in to water/methanol mixture (ratio 1 : 5). The grafted sample has been separated by filtration, dried and weighed.

Separation of homopolymer

Poly(vinyl sulfonic acid) remained in the filtrate. To the filtrate a pinch of hydroquinone has been added and then it is concentrated by distillation under reduced pressure. This concentrated solution is poured into the pure methanol to precipitate the poly(vinyl sulfonic acid). The poly(vinyl sulfonic acid) is separated dried and weighed.

Estimation of grafting parameters

The graft copolymer has been characterized by following parameters.[20]

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

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

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

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

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

Study of properties

Flocculation

In 1-L beaker, 200 cc of 1% wt. coal suspension (in water) was taken and the beaker was placed on floc-

culator dipping the stirrer blade in the suspension. Under a low stirring condition, required quantity of sample solution was added to beaker to make predetermined dose with respect of suspension volume. After the addition of sample solution, the suspension was stirred at a constant speed for 15 min. The flocs were allowed to settle down for half an hour. Clean supernatant liquid was drawn from a depth of 1.0 cm and its turbidity was measured using a digital nephelometer (DIGITAL NEPHELOMETER MODEL 341 (EI) supplied by ISO-TECH SYSTEM) to express the turbidity in nephelometric unit (N.T.U.).

Metal ion uptake

The metal ion sorption studies have been carried out on graft copolymer of different compositions, which have been synthesized by varying the concentration of vinyl sulfonic acid from $2.6 \times 10^{-2} - 8.0 \times 10^{-2}$ mol dm^{-3}. For this 0.02 g of graft copolymer has been taken in 10 mL of metal ion solution of known concentration and kept for 24 h. The strength of unabsorbed metal ion solution has been determined by standard method. For metal ion sorption studies we have chosen three metal ions i.e., Ni^{2+}, Pb^{2+}, and Zn^{2+}. Sorption behavior of polymeric backbone and graft copolymer for three metals ions have been investigated by using following parameters.[21]

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

$$\text{Partition coefficient}(K_d) = \frac{\text{Amount of metal ion in polymer}}{\text{Amount of metal ion left in solution}} \times \frac{\text{Vol. of solution (ml)}}{\text{Wt. of dry Polymer (gm)}}$$

$$\text{Retention capacity}(Q_r) = \frac{\text{Amount of metal ion in polymer (mEq)}}{\text{Wt. of dry polymer (gm)}}$$

Swelling test

For swelling study, different samples of graft copolymer have been synthesized at different concentrations of vinyl sulfonic acid (VSA) from 2.6×10^{-2} to 8.0×10^{-2} mol dm^{-3}. The preweighed samples (0.02 g) of each were immersed in 20 mL of triple distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The swollen samples were then removed from triple distilled water, quickly wiped with filter paper to
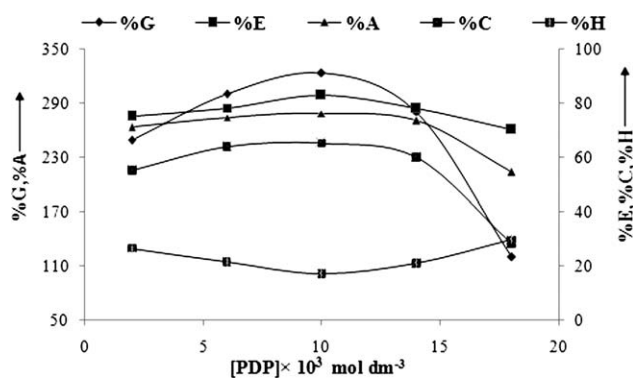
Figure 1 Effect of PDP concentration [VSA] = 4.6×10^{-2} mol dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, Time = 120 min, [AOH] = 1.0 g dm^{-3}, [TU] = 3.2×10^{-3} mol dm^{-3}, Temp. = 40°C.

remove droplets on the surface and weighed. The percent swelling (P_s) and swelling ratio (S_r) have been calculated by using following expressions.[22]

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

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

Resistance to biodegradability

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

Method of characterization of alginate-*g*-vinyl sulfonic acid

IR Spectroscopy

The IR spectra of alginate and grafted samples have been recorded with JASCO FT/IR-5300 model in the range 500 to 4000 cm^{-1}.

Thermogravimetric analysis

The thermograms have been recorded on NETZSCH – STA 409C/CD thermal analyzer from 0°C to 1400°C temperature range and with a heating rate of 15°C/min in nitrogen atmosphere.

RESULTS AND DISCUSSIONS

Determination of optimum grafting conditions

The optimum reaction conditions for maximum percentage of grafting of vinyl sulfonic acid onto alginate by using potassium peroxydiphosphate (PDP)/

TU as redox system in the presence of hydrogen ion (H$^+$) have determined.

Effect of concentration of peroxydiphosphate

The effect of peroxydiphosphate concentration on graft copolymerization has been studied at different concentration of peroxydiphosphate and results are presented in Figure 1. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration of peroxydiphosphate from 2.0 $\times 10^{-3}$ to 10×10^{-3} mol dm^{-3}. The increasing pattern has been found due to production of more primary free radicals R$_1$S° and HPO$_4^{\bullet-}$, which attack on the alginate molecules creating more free radical sites onto which monomer addition takes place.

Effect of concentration of thiourea

The effect of thiourea on grafting parameters has been studied by varying the concentration of thiourea from 1.6×10^{-3} to 4.8×10^{-3} mol dm^{-3}. It has been observed that grafting ratio, add on, and efficiency increases on increasing the concentration of thiourea up to 3.2×10^{-2} mol dm^{-3}. The increase in the grafting parameters was attributed to the increase in the rate of production of primary free radicals with an increase in the thiourea concentration up to 3.2×10^{-2} mol dm^{-3}. After this concentration, the concentration of peroxydiphosphate became less than that of TU, so the rate of production of primary free radicals decreased; therefore, a decrease in the grafting parameters was observed. The results are given in Table I.

Effect of concentration of alginate

The effect of concentration of alginate has been observed with an aim to study the effect of its concentration (from 0.6 to 1.6 mol dm^{-3}) on grafting parameters and results are shown in Figure 2. It is observed that the grafting parameters decrease continuously on increasing the concentration of alginate, this may be due to greater availability of grafting site at alginate backbone.

TABLE I
Effect of Tu Concentration

[TU]$\times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
1.6	205.1	76.3	67.2	44.9	23.6
2.4	266.6	78.8	72.1	54.4	21.1
3.2	323.7	82.7	76.4	65.3	17.1
4.0	298.7	88.7	74.9	56.3	11.3
4.8	204.1	62.1	67.1	54.8	37.8

[VSA] = 4.6×10^{-2} mol dm^{-3}, [PDP] = 10×10^{-3} mol dm^{-3}, [AOH] = 1.0 g dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, Temp. = 40°C, Time = 120 min.
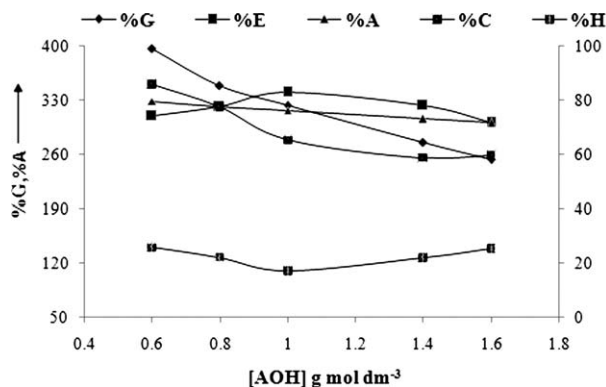
Figure 2 Effect of AOH concentration [VSA] = 4.6×10^{-2} mol dm^{-3}, [PDP] = 10×10^{-3} mol dm^{-3}, Time = 120 min, [H$^+$] = 4×10^{-3} mol dm^{-3}, [TU] = 3.2×10^{-3} mol dm^{-3}, Temp. = 40°C.

Effect of concentration of hydrogen ion

The effect of the hydrogen-ion concentration on the grafting parameters was studied through the variation of the concentration of hydrogen ion from 2×10^{-3} to 6×10^{-3} mol dm^{-3}. The grafting ratio, add-on, and efficiency increased when the hydrogen-ion concentration increased from 2×10^{-3} to 5×10^{-3} mol dm^{-3} but beyond this range, these parameters decreased. The increase in the grafting parameters with the hydrogen-ion concentration up to 5×10^{-3} mol dm^{-3} was due to protonation of TU, and these protonated species reacted with the active species of the PDP ion (H$_2$P$_2$O$_8^{-2}$) to give more primary free radicals; hence, an increase in the values of these parameters was observed:
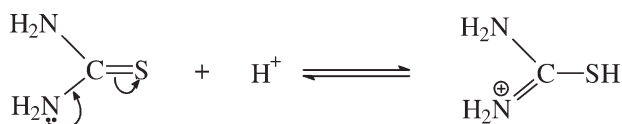
However, beyond 5×10^{-3} mol dm^{-3}, these parameters decreased with an increase in the hydrogen concentration, and this was attributed to the formation of less active species[23] of PDP such as H$_5$P$_2$O$_8^+$ and H$_6$P$_2$O$_8^{2+}$. The results are shown in Table II.

TABLE II
Effect of H$^+$ Ion Concentration

[H$^+$] $\times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
2	243.9	70.8	70.9	57.5	29.1
3	273.3	78.8	73.2	57.9	21.1
4	323.7	82.7	76.4	65.3	17.1
5	347.8	87.7	77.6	66.4	12.2
6	198.1	72.1	66.4	45.8	27.9

[VSA] = 4.6×10^{-2} mol dm^{-3}, [PDP] = 10×10^{-3}, Time = 120 min, [AOH] = 1.0 g dm^{-3}, [TU] = 3.2×10^{-3} mol dm^{-3}, Temp. = 40°C.
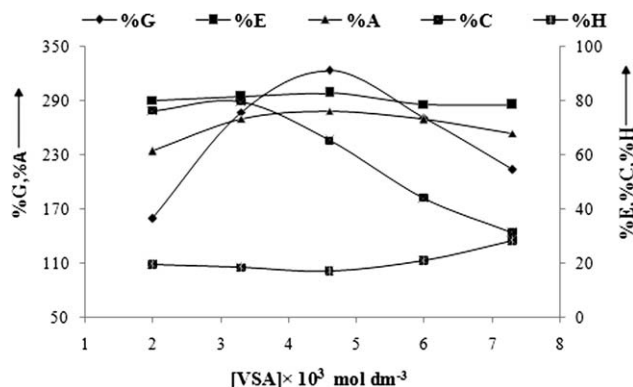
Figure 3 Effect of VSA concentration [TU] = 3.2×10^{-3} mol dm^{-3}, [PDP] = 10×10^{-3} mol dm^{-3}, [AOH] = 1.0 g dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, Temp. = 40°C, Time = 120 min.

Effect of concentration of vinyl sulfonic acid

The effect of concentration of vinyl sulfonic acid on grafting parameters has been investigated by varying the concentration of vinyl sulfonic acid from 2.0×10^{-2} to $7.3.0 \times 10^{-2}$ mol dm^{-3} and results are presented in Figure 3. It has been observed that grafting ratio, add on and efficiency increase on increasing the concentration up to 4.6×10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease. However the formation of homopolymer shows a reverse trend with respect to grafting efficiency. This behavior is attributed to accumulation of monomer molecules at close proximity of polymeric backbone. The monomer molecules, which are at the immediate vicinity of reaction sites, become acceptors of alginate macro radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighboring molecules. But on further increasing the concentration of vinyl sulfonic acid, it is found that decrease in grafting parameter is observed which is due to increase viscosity of the medium, which in turn hinders the movement of free radicals.

Effect of temperature

The effect of temperature on grafting parameters has been studied from 30 to 50°C. It has been observed that grafting ratio, add on, and efficiency increases continuously on increasing the temperature. The increment in grafting ratio, add on, and efficiency is attributed to the fact that the rate of production of primary free radicals increases and movement of vinyl sulfonic acid to alginate free radicals also increased which increase the value of grafting parameters. The results are shown in Table III.

Effect of time

The effect of time period on grafting parameters has been studied by varying the time period of the
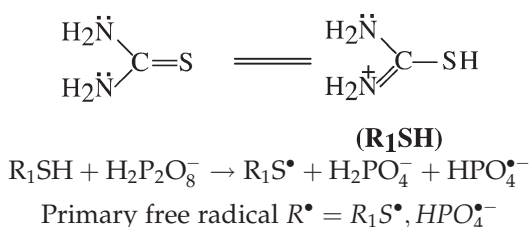
TABLE III
Effect of Temperature

Temp. (°C)	%G	%E	%A	%C	%H
30	289.1	77.3	74.2	62.4	22.6
35	306.5	82.2	75.3	63.3	17.7
40	323.7	82.7	76.4	65.3	17.1
45	281.2	74.1	73.7	63.3	25.8
50	213.8	64.8	68.1	53.4	33.1

[VSA] = 4.6×10^{-2} mol dm^{-3}, [PDP] = 10×10^{-3} mol dm^{-3}, [AOH] = 1.0 g dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, [TU] = 3.2×10^{-2} mol dm^{-3}, Time = 120 min.
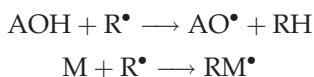
reaction from 60 to 180 min. It has been observed that grafting ratio, add on, and efficiency increase continuously with increase in time period which leads to increase in the rate of production of radicals, hence increase in grafting parameters has been observed. The results are shown in Figure 4.

Mechanism

It is assumed that in the presence of hydrogen ion thiourea may be protonated which reacts with peroxydiphosphate to give free radicals $R_1S^\bullet$ and $HPO_4^{\bullet-}$. These radicals extract hydrogen atoms from alginate molecules producing alginate macro free radicals. The monomer molecules which are in close vicinity of the reaction sites, become acceptor of alginate radicals resulting in chain initiation and thereafter themselves become free radicals donor to neighboring molecules, thus grafted chain grows. Termination of chains by coupling yields graft copolymer. The mechanism can be represented as
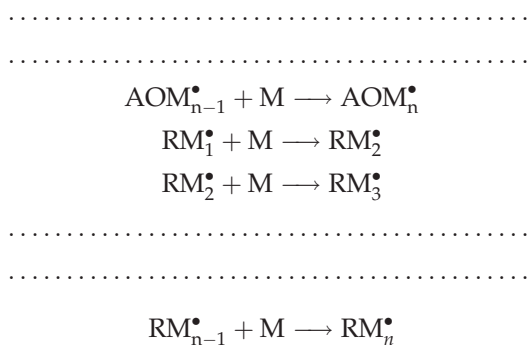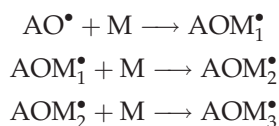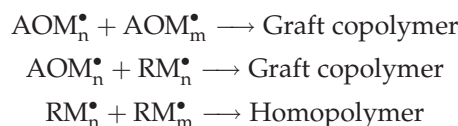
$$H_2\ddot{N}\diagdown C=S \quad \Longleftrightarrow \quad H_2\ddot{N}\diagdown \underset{+}{C}-SH$$
$$H_2\ddot{N}\diagup \qquad\qquad H_2\ddot{N}\diagup$$

(R$_1$SH)

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

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

Initiation

$$AOH + R^\bullet \longrightarrow AO^\bullet + RH$$
$$M + R^\bullet \longrightarrow RM^\bullet$$

[Where AOH = alginate and M = Vinyl sulfonic acid]

Propagation

$$AO^\bullet + M \longrightarrow AOM_1^\bullet$$
$$AOM_1^\bullet + M \longrightarrow AOM_2^\bullet$$
$$AOM_2^\bullet + M \longrightarrow AOM_3^\bullet$$

. . . .
. . . .

$$AOM_{n-1}^\bullet + M \longrightarrow AOM_n^\bullet$$
$$RM_1^\bullet + M \longrightarrow RM_2^\bullet$$
$$RM_2^\bullet + M \longrightarrow RM_3^\bullet$$

. . . .

. . . .

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

Termination

$$AOM_n^\bullet + AOM_m^\bullet \longrightarrow \text{Graft copolymer}$$
$$AOM_n^\bullet + RM_n^\bullet \longrightarrow \text{Graft copolymer}$$
$$RM_n^\bullet + RM_m^\bullet \longrightarrow \text{Homopolymer}$$

Evidence of grafting

IR spectroscopy

The infra red spectra have been utilized to prove grafting, for this IR spectra of alginate and alginate-*g*-vinyl sulfonic acid have been recorded in the range of 500 to 4000 cm^{-1}. On comparing the IR spectra of alginate Figure 5 and alginate-*g*-vinyl sulfonic acid Figure 6, a band at 3452.3 cm^{-1} is due to OH stretching vibration in the spectrum of alginate. It is observed that there is variation in intensity of OH stretching vibration and shifting of this peak from 3452.3 to 3447.3 cm^{-1} appeared in alginate-*g*-vinyl sulfonic acid respectively, indicating the participation of hydroxyl groups in chemical reaction. The graft copolymerization is further confirmed by characteristic absorption band of —SO$_2$—O— stretching vibration at 1113.1 cm^{-1} of monomer molecule. The appearance of additional peaks in spectrum of graft
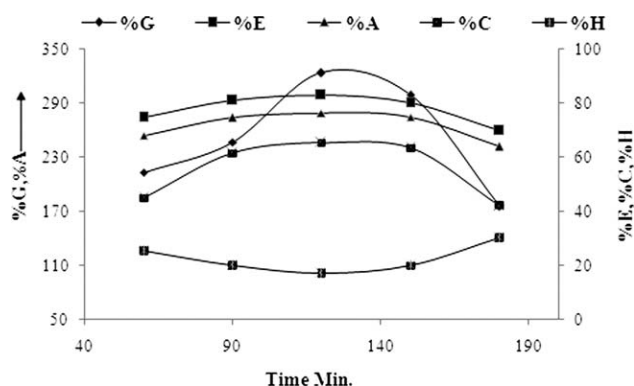
Figure 4 Effect of time [VSA] = 4.6×10^{-2} mol dm^{-3}, [PDP] = 10×10^{-3} mol dm^{-3}, [AOH] = 1.0 g dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, [TU] = 3.2×10^{-3} mol dm^{-3}, Temp. = 40°C.
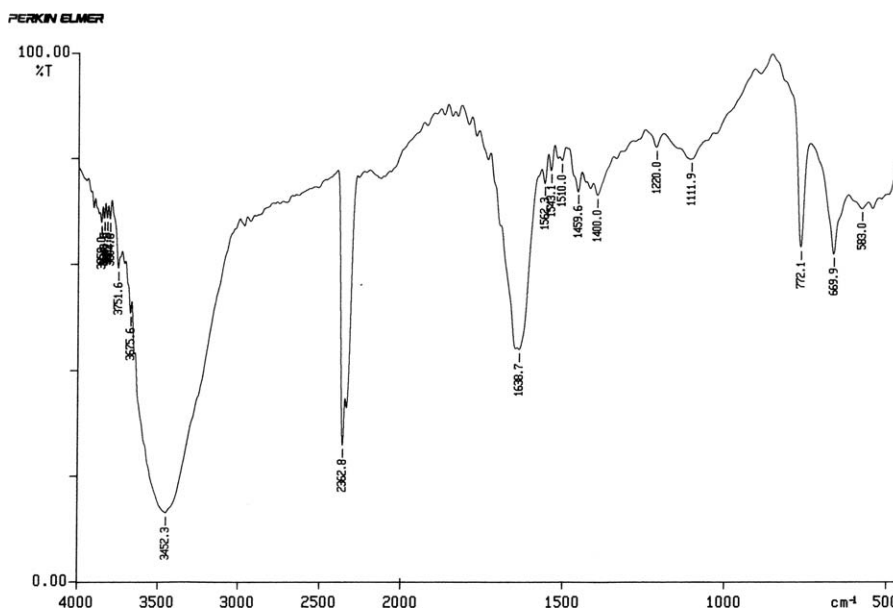
Figure 5 IR spectrum of alginate.

copolymer and shifting of OH stretching vibration appeared in the spectrum of alginate from the spectrum of alginate-g-vinyl sulfonic acid showed that grafting might have taken place on OH sites of alginate.

Thermogravimetric analysis

Thermogravimetric analysis curve of alginate shows single step degradation. The 0.4% weight loss at 71.4°C might be due to loss of absorbed water. It starts to degrade at 100.0°C. The polymer decomposition temperature (PDT) has been found at 200.0°C as presented in Figure 7. The rate of weight loss increases with increase in temperature from 200.0°C to 250.0°C and thereafter decreases and attains a maximum value at about 252.8°C. T_{max}, temperature at which maximum degradation occurred, is 211.3°C which is also confirmed by the peak appeared in DTA curve of alginate. The final decomposition temperature (FDT) and integral decomposition temperature (IPDT) have been found at 900.0°C and 267.3°C, respectively. But in case of alginate-g-vinyl sulfonic acid, the weight loss 2.4% at about 42.5°C might be due to loss of absorbed water. The polymer decomposition temperature (PDT) has been found at 146.5°C.
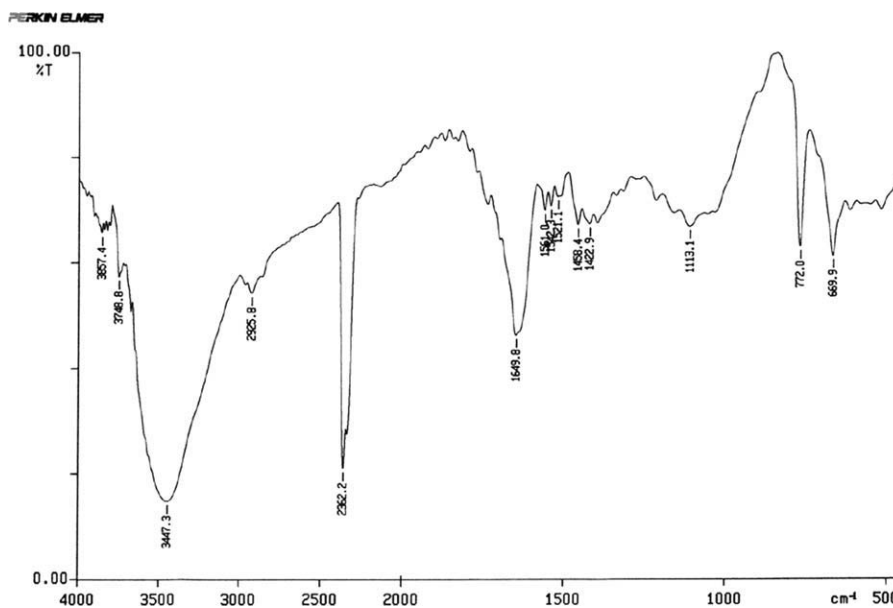

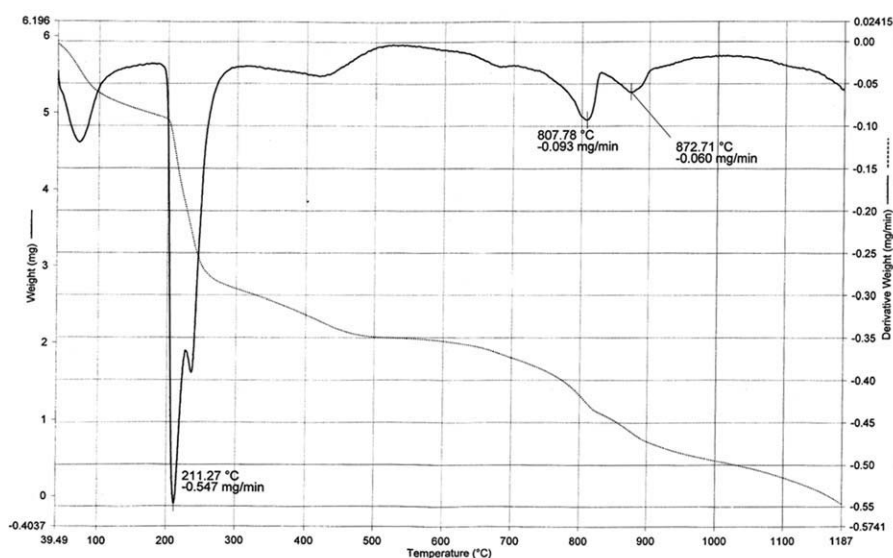**Figure 6** IR spectrum of alginate-g-vinyl sulfonic acid.

Figure 7 Thermogravimetric trace of alginate.

Alginate-*g*-vinyl sulfonic acid Figure 8 shows four step degradations. It has been found that degradation of alginate-*g*-vinyl sulfonic acid starts at about 100°C temperature (presented in Fig. 10). The rate of weight loss increases with increase in temperature from 105°C to 152.5°C and there after decreases and attains maximum at about 732.35°C. First T_{max}, 207.02°C is due to elimination of COO⁻ groups which also confirmed by a peak appeared at about 220.5°C DTA curve of alginate. The second T_{max}, is 359.53°Cis due to elimination of OH (Leaving from alginate) group, confirmed by a peak appeared at about 370.62°C in

DTA curve. The third T_{max} at 732.35°C is due to elimination of SO₂ molecule from pendent chains attached to alginate confirmed by a peak appeared at about 370.62°C in DTA curve. The Fourth T_{max} at 1083.01°C is due to elimination of OH group from, confirmed by a peak appeared at about 1110.25°C in DTA curve Figure 9. The integral procedural decomposition and final decomposition temperature have been found at about 428.06°C and 1083.01°C, respectively. On comparing the thermograms of parent backbone (alginate) and graft copolymer (alginate-*g*-vinyl sulfonic acid), it has been observed that final and integral procedural
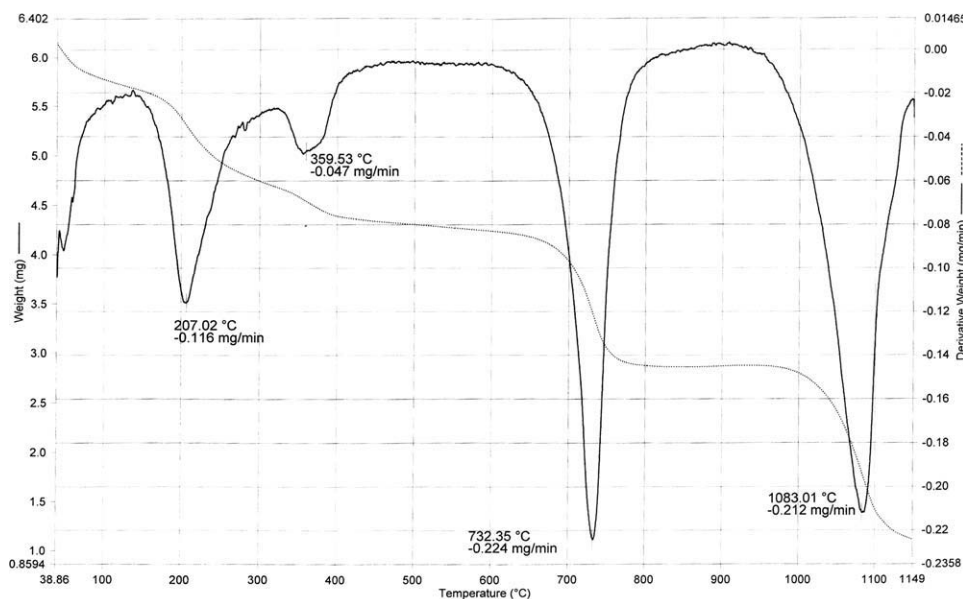

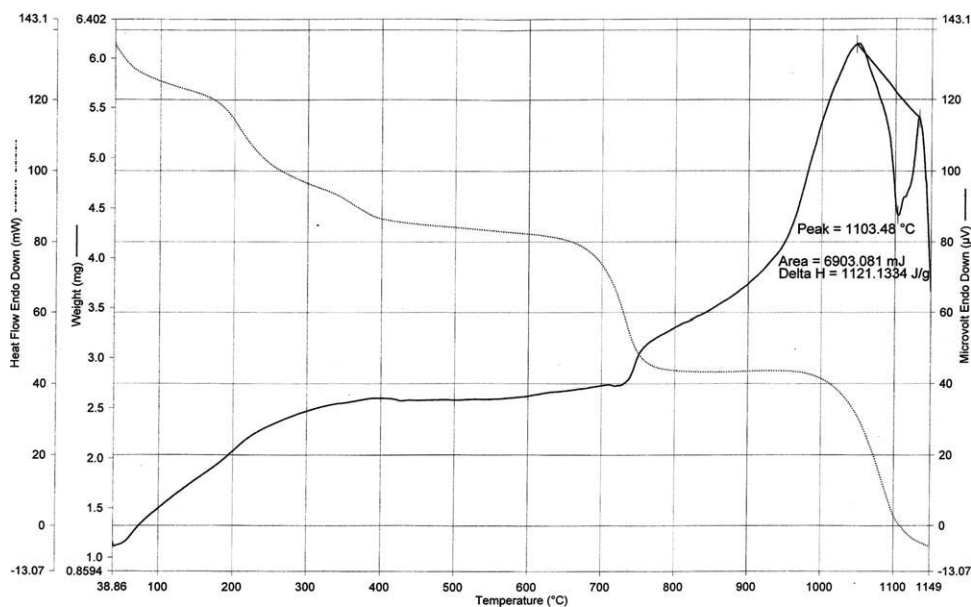**Figure 8** Thermogravimetric trace of alginate-*g*-vinylsulfonic acid.

Figure 9 Differential thermal trace of alginate-*g*-vinylsulfonic acid.

decomposition have been found to be higher for graft copolymer. This indicates that graft copolymer is thermally stable than backbone.

Study of the properties

Flocculating properties

Plots of supernatant turbidity versus polymer dosage for coking and noncoking coals are given in Figure 10. It has been found that grafted copolymer (alginate-*g*-vinyl sulfonic acid) gives better performance by showing lower turbidity than alginate itself. This phenomenon could be explained by considering bridging mechanism.[24] In grafted copolymer, the dangling of poly(vinyl sulfonic acid) chains have better approachability to the contaminant coal particles hence increases its flocculation capability. The difference in turbidity value in coking coal and noncoking coal in coal suspension is due to difference in negative charge density, which is higher in noncoking coal in aqueous solution.[25] Thus, by grafting of poly vinyl sulfonic acid onto alginate, efficient flocculants have been obtained and it could be used for the treatment of coal waste water.

Metal ion sorption study

The results of sorption behavior of alginate and its grafted polymer with vinyl sulfonic acid have been determined in terms of different parameters and the results are given in Table IV. It has been observed that the values of percent ion uptake (P_u), partition coefficient (K_d) and retention capacity (Q_r) increase directly as percent grafting increases, which might be due to the fact that as grafting increases, the den-

sity of sorption sites for metal ions are increased due to availability of additional functional groups of poly pendent chain of monomer, which further increases with increased grafting. Results also show that Zn^{2+} was most uptakable in comparison to two metal ions of them, which have been used.

Swelling test

An increase in weight of graft copolymer has been recorded by performing swelling test. The results have been summarized in Table V, which indicates that swelling ratio and swelling percent depend on the concentration of monomer used while grafting. Since vinyl sulfonic acid is a hydrophilic monomer, it increases the water retention character of graft
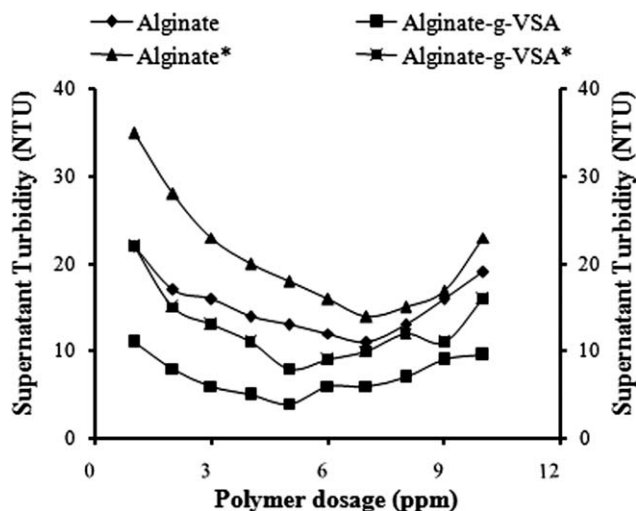

Figure 10 Effect of polymer dosage on turbidity for non-coking and noncoking coals*.

TABLE IV
Metal Ion Uptake

Sample	[VSA] $\times 10^2$ mol dm^{-3}	%G	Percent uptake (Pu)			Partition coefficient (Kd)			Retention capacity (Qr)		
			Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
AOH	–	–	3.3	2.3	1.3	18.4	15.4	5.9	2.0	1.3	0.5
A	2.6	177.7	14.4	10.0	5.4	94.2	63.3	28.2	2.1	5.7	2.1
B	4.0	229.7	16.7	11.4	5.8	100.2	67.2	29.1	2.4	6.4	2.4
C	5.3	243.1	18.2	13.1	6.5	113.3	76.4	31.5	2.7	7.1	2.7
D	6.6	333.4	14.6	10.6	5.1	84.2	62.1	27.4	2.3	6.8	2.3
E	8.0	205.7	14.3	10.4	4.9	82.3	60.4	27.1	2.0	6.7	2.1

[TU] = 3.2×10^{-3} mol dm^{-3}, [PDP] = 10×10^{-3} mol dm^{-3}, [AOH] = 1.0 g dm^{-3}, [H$^+$] = 4×10^{-3} mol dm^{-3}, Temp. = 40°C, Time = 120 min.
AOH, alginate; A, B, C, D, E, graftcopolymers.

copolymer. On increasing the concentration of vinyl sulfonic acid, grafting is increased, which may result into coiling network of poly(vinyl sulfonic acid), thus imbibes more water. The presence of amide group of substrate and a hydrophilic monomer, both factors are responsible for good swelling capacity of graft copolymer. Swelling percent is increased with increased percent grafting because on increasing vinyl sulfonic acid concentration, pendant chain of poly(vinyl sulfonic acid) grows thereby increasing the swelling capacity of graft copolymer.

Resistance to biodegradability

From efflux time of polymer solution (t) and that of solvent 1.0M NaNO$_3$ (t_o), relative viscosity η_{rel}= (η/η_0) was obtained. It has been observed that relative viscosity of alginate-*g*-vinyl sulfonic acid is lower than alginate (Fig. 11). This might be due to presence of grafted chains which make the molecule more flexible and reduce the viscosity drastically.[26] Alginate 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. 11, Line A). The graft copolymer solution was subjected for

TABLE V
Swelling Capacity of Alginate-*g*-vinyl Sulphonic Acid

Sample code	[VSA] $\times 10^2$ mol dm^{-3}	%G	P_S	S_R
C$_{N1}$	2.6	177.7	115	1.15
C$_{N2}$	4.0	229.7	200	2.00
C$_{N3}$	5.3	243.1	280	2.80
C$_{N4}$	6.6	333.4	350	3.50
C$_{N5}$	8.0	205.7	405	4.05

[AOH] = 1.0 g dm^{-3}; [PDP] = 12×10^{-3} mol dm^{-3}, [TU] = 3.2×10^{-3} mol dm^{-3}; [VSA] = 5.3×10^{-2} mol dm^{-3}; [H$^+$] = 4×10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40°C.
Where C$_N$ indicates the graft copolymer Alginate-*g*-vinyl sulphonic acid.

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. 11, Line B). These results show that the graft copolymer is less susceptible to biodegradation and results have also been reported by others.[27] This is in an agreement with the fact that by incorporating relatively poly(vinyl sulfonic acid) chains in graft copolymer it can be made less susceptible to bacterial attack.[28]

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

CONCLUSIONS

The thermal data show that the synthesized graft copolymer is thermally more stable than pure alginate. The synthesized graft copolymer i.e., alginate-*g*-vinyl sulfonic acid shows better results for swelling, metal ion uptake, flocculating and resistance to biodegradability properties in comparison to alginate, this could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic
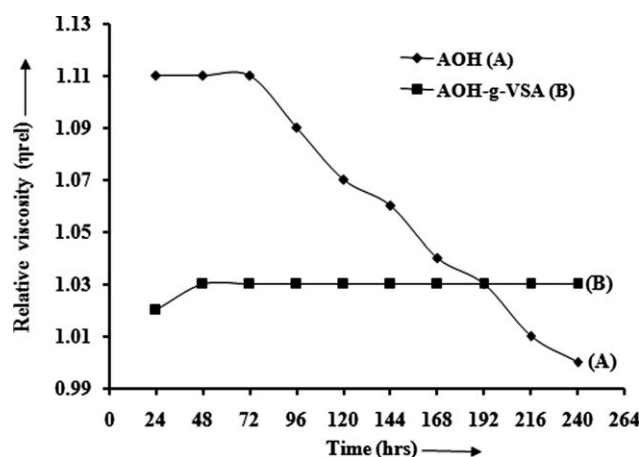

Figure 11 Relative viscosity vs. time period to study biodegradation of alginate and graft copolymer.

data confirm that the grafting of vinyl sulfonic acid might have taken place at hydroxyl group, which is supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft co-polymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well industrially.

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