Alginic Acid-*g*-Poly(*N*-vinylformamide) Graft Copolymer: Synthesis, Characerization, Swelling, and Flocculation Property

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ABSTRACT: The graft copolymer of *N*-vinylformamide with alginic acid was synthesized by free radical polymerization using potassium peroxymonosulphate and thiourea as redox pair in inert atmosphere. The optimum conditions for maximum grafting have been determined by varying the concentrations of *N*-vinylformamide, potassium peroxymonosulphate, thiourea, sulfuric acid, alginic acid as well as time duration and temperature. The grafting parameters increase up to the certain concentrations of *N*-vinylformamide, potassium peroxymonosulhate, thiourea, and hydrogen ion while thereafter grafting parameters decrease. The effect of alginic acid concentration on grafting parameters has been observed to decrease continuously. It has also been found that grafting parameters increase up to certain time and temperature, respectively, and thereafter decrease. The swelling properties of graft copolymer in terms of swelling ratio and percent swelling are investigated. Flocculation property of pure and grafted sample for both coking and noncoking coals is also investigated for the treatment of coal mine waste water. The graft copolymer has been characterized by Fourier transform infrared spectroscopy as well as thermogravimetic analysis. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1400–1407, 2011

Key words: graft copolymer; alginic acid; *N*-vinylformamide; swelling; flocculation

INTRODUCTION

The phenomenal growth in the field of functional materials[1,2] based on graft copolymers has become increasingly important in industrial applications over the past decades. To increase the paramount contributions towards their improved industrial applications, various graft copolymers have been synthesized in our laboratory.[3,4] In the same way, the present study concerned with the synthesis of a new type of graft copolymer, has been made using polymeric backbone of alginic acid (AOH). Alginic acid, also called algin, or alginate, is a naturally occurring colloidal hydrophilic polysaccharide obtained from the various species of brown seaweed (phaeophyceae).[5,6] It is a linear copolymer consisting mainly the residue of β-1, 4-linked D-mannuronic acid and α-1, 4-linked L-guluronic acid.[7–9] It has a broad range of applications in pharmaceutical,[10,11] biomedical,[12] and agricultural areas.[13,14] It also plays an important role as an adduct product[15] to food

due to its property forming highly viscous solution. Some workers reported that Alginic acid is easily capable to form a gel, a well stable system in the presence of divalent cation as the calcium ion[16,17] as well as composite gel beads with tamarind gum.[18] Although AOH possesses good properties and various industrial applications, it suffers from its drawbacks, i.e., biodegradability[19–22] which limits its uses considerably. Grafting of vinyl monomer, the method, on to polymeric backbone of alginic acid not only improves the drawbacks but also increases its properties such as swelling and flocculation because the additional properties of vinyl monomer are superimposed. *N*-vinylformamide (NVF), a key compound in synthesis of cationic polymers,[23] is hydrophilic and low toxic in nature. It has potential interests in a number of areas such as petroleum recovery from oil wells, water treatment, and effective drag reducing agent and the major applications such as dry and wet strength for paper making.[24–29] Prompted by the applications of NVF and AOH, hitherto unreported graft copolymer viz. graft copolymer (alginic acid-*g*-*N*-vinylformamide) has been prepared by using potassium peroxymonosulphate (PMS)/thiourea (TU) redox system and some of the properties like swelling capacity and flocculation studies has been investigated.

EXPERIMENTAL

Materials

NVF (Sigma-Aldrich Co. Ltd, Gillingham, Dorset, SP8 4XT, UK) was distilled under reduce pressure at 14 mmHg and 55°C and only middle fraction was used. AOH was purchased from (Sigma-Aldrich Co. Ltd, Gillingham, Dorset, SP8 4XT, UK). PMS (Sigma-Aldrich Co. Ltd, Gillingham, Dorset, SP8 4XT, UK) and TU (E. Merck, India) were used as such. For maintaining hydrogen ion concentration, sulfuric acid (E. Merck, India) is used. All the solutions were prepared in triple distilled water. The other chemicals used were of analytical grade and used as such without further purification. For the flocculation, coking and noncoking coals were received from steel plant Bokaro, India.

Procedure for graft copolymerization

All the reactions were carried out in nitrogen atmosphere. For each experiment, alginic acid solution has been prepared by adding weighed amount of alginic acid into the reactor containing triple distilled water. The calculated amount of NVF (8×10^{-2} to 24×10^{-2}) mol dm^{-3}, PMS (2×10^{-3} to 18×10^{-3}) mol dm^{-3}, TU (1.2×10^{-3} to 4.4×10^{-3}) mol dm^{-3}, and sulfuric acid (2×10^{-3} to 6×10^{-3}) mol dm^{-3} solutions have been added to the reactor at constant temperature (range from 30 to 50°C) and a slow stream of purified nitrogen gas is passed. After 30 min, a known amount of deoxygenated PMS (2×10^{-3} to 18×10^{-3}) mol dm^{-3} solution is added to initiate the reaction, and allowed to continue for 2 h. After desired time period, the reaction was stopped by letting air into the reactor. The grafted sample has been precipitated by pouring reaction mixture into water/methanol mixture (ratio 1 : 5). The grafted sample has been separated by filtration and then dried and weighed.

Separation of homopolymer

Poly(*N*-vinylformamide) is remained in the filtrate. To the filtrate a pinch of hydroquinone is added and then it is concentrated by distillation under reduced pressure. This concentrated solution is poured into the pure methanol to find out the precipitate of poly(*N*-vinylformamide). The poly(*N*-vinylformamide) is separated, dried, and weighed.

Estimation of grafting parameters

The graft copolymer has been characterized by following grafting parameters[30,31]:

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

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

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

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

$$\text{Homopolymer } = 100 - \%\,\text{Grafting efficiency}$$

Method of characterization of Alginic acid/alginic acid-*g*-N-vinylformamide

IR spectroscopy

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

Thermogravimetric analysis

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

Study of properties

Swelling

The swelling capacity of different samples of graft copolymer has been investigated. The samples of graft copolymer have been synthesized at different concentrations NVF (8×10^{-2} to 24×10^{-2}) mol dm^{-3}. The preweighed sample (0.02 g of each) was immersed in 20 mL of triple-distilled water and kept undisturbed for 10 h at room temperature until equilibrium swelling was reached. The surface water on swollen sample was then removed by pressing it between twofolds of filter paper and weighed. The percent swelling (Ps) and swelling ratio (Sr) have been calculated by using following expressions.[32,33]

$$\text{Swelling ratio (Sr)}$$
$$= \frac{\text{Weight of swollen sample} - \text{weight of dry sample}}{\text{weight of dry sample}}$$

$$\text{Percent swelling (PS)} = \text{Swelling ratio (Sr)} \times 100$$

Flocculation

In 1.0 L beaker, 200 cc of 1% wt coal suspension was taken. The beaker was placed on flocculator dipping the stirrer blade 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.
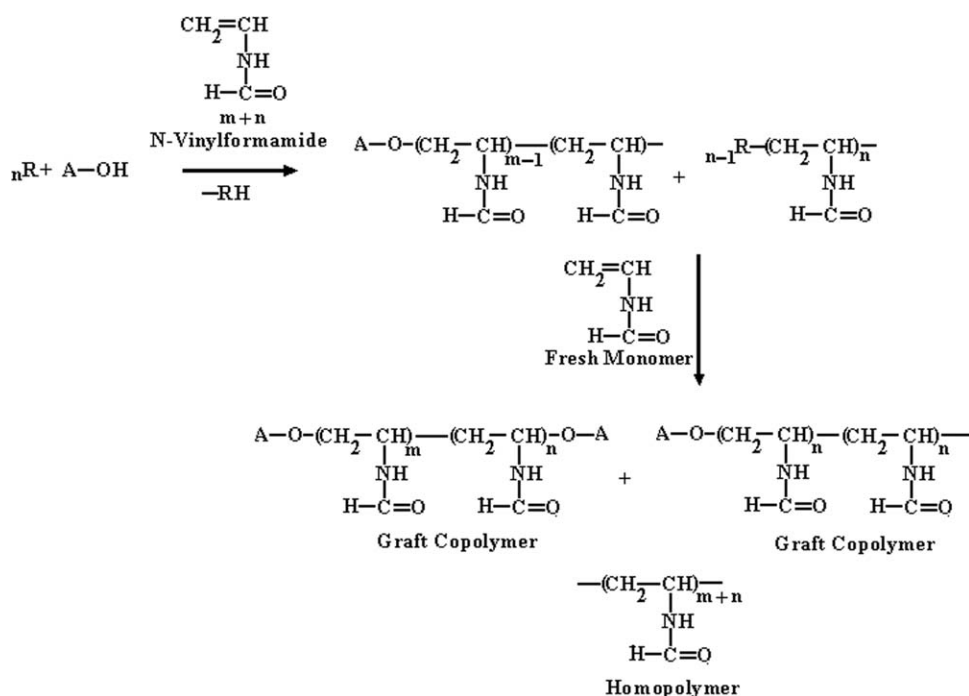
Figure 1 Scheme of formation of graft copolymer.

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 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, Varanasi, India] to express the turbidity in nephelometric unit (N.T.U.).

RESULTS AND DISCUSSIONS

Determination of optimum grafting conditions

The optimum reaction conditions for affording maximum percentage of grafting as shown figure 1 have been established in the case of grafting of NVF onto AOH by using PMS and TU redox system in the presence of sulfuric acid with the effect of time and temperature.

Effect of [peroxymonosulphate]

The effect of PMS concentration on grafting parameters has been studied by varying the concentration of PMS from 2×10^{-3} to 18×10^{-3} mol dm^{-3}. The results are presented in Table I. The grafting ratio, add on and efficiency have been found to increase on increasing the concentration of PMS from 2×10^{-3} to 10×10^{-3} mol dm^{-3}. The increment in grafting parameters is due to the progressive reduction of PMS by TU, which produces primary free radicals i.e., $R^{\bullet} = R_1S^{\bullet}$ and $SO_4^{\bullet-}$.[34] These primary free radicals interact with NVF and AOH molecules to produce macro-radicals, which propagate the growing grafted chains giving rise to the formation

of more number of active sites on polymeric backbone. However, beyond cited range of concentration of PMS i.e., 2×10^{-3} to 10×10^{-3} mol dm^{-3}, all these parameters decrease which is attributed due to premature termination of growing grafted chains.[35]

Effect of [thiourea]

The variation of TU concentration from 1.2×10^{-3} to 4.4×10^{-3} mol dm^{-3} reveals that of grafting ratio, add on and efficiency increase on increasing the TU concentration up to 2.8×10^{-3} mol dm^{-3} because of availability of more primary free radicals ($R^{\bullet} = R_1S^{\bullet}$ and $SO_4^{\bullet-}$), which is formed due to reduction of PMS by TU.[36] However, on further increasing the concentration of TU from 2.8×10^{-3} to 4.4×10^{-3} mol dm^{-3}, the decrement in grafting parameters has been found which is probably due to premature termination of NVF radicals which cause to give more to more homopolymer. The results are given in Figure 2.

TABLE I
Effect of [Peroxymonosulphate]

[PMS] $\times 10^3$ mol dm^{-3}	%G	%E	%A	%C	%H
2	195.0	60.8	74.6	42.8	39.1
6	216.8	68.9	76.0	40.4	31.0
10	320.4	74.4	76.2	37.8	25.5
14	292.9	70.6	74.7	48.4	29.3
18	263.1	57.2	72.4	40.4	42.7

[AOH] = 1.0 g g dm^{-3}; [NVF] = 16×10^{-2} mol mol dm^{-3}; Time = 120 min; [TU] = 2.8×10^{-3} mol mol dm^{-3}; [H$^+$] = 4×10^{-3} mol mol dm^{-3}; Temp. = 40°C.
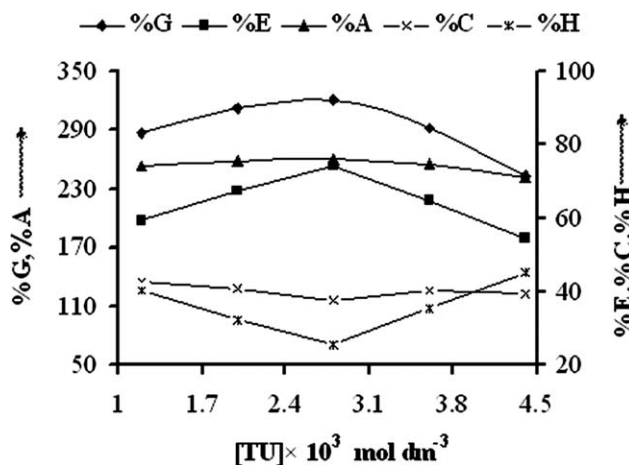
Figure 2 Effect of [thiourea]. [AOH] = 1.0 g dm^{-3}; [NVF] = 16 × 10^{-2} mol dm^{-3}; Time = 120 min; [PMS] = 10 × 10^{-3} mol dm^{-3}; [H$^+$] = 4 × 10^{-3} mol dm^{-3}; Temp. = 40°C.

Effect of [alginic acid]

The effect of concentration of AOH has been observed with an aim to study the effect of its concentration (from 0.6 to 1.4) g dm^{-3} on grafting parameters. The results are presented in Figure 3. It is obtained that the grafting parameters decrease continuously on increasing the concentration of AOH. This is due to increment in viscosity of the reaction medium which hinders the movement of free radicals.

Effect of [hydrogen ion]

The concentration of hydrogen ion plays an important role during the reaction. The effect of hydrogen ion concentration has been studied by varying the concentration from 2.0 × 10^{-3} mol dm^{-3} to 6.0 × 10^{-3} mol dm^{-3}. It has been observed from
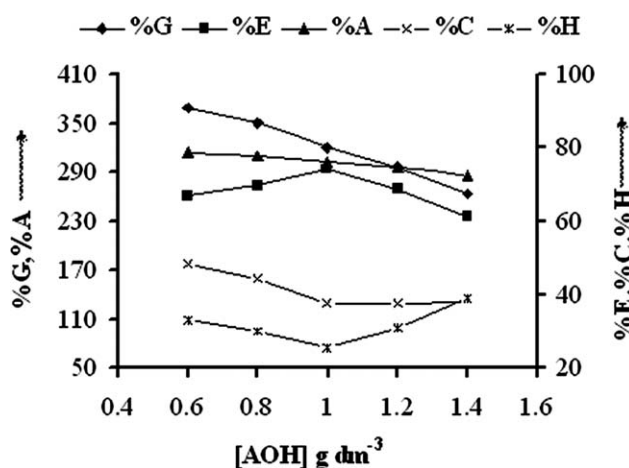
Figure 3 Effect of [alginic acid]. [PMS] = 10 × 10^{-3} mol dm^{-3}; [NVF] = 16 × 10^{-2} mol dm^{-3}; Time = 120 min; [TU] = 2.8 × 10^{-3} mol dm^{-3}; [H$^+$] = 4 × 10^{-3} mol dm^{-3}; Temp. = 40°C.

TABLE II
Effect of [Hydrogen Ion]

[H$^+$] × 10^3 mol dm^{-3}	%G	%E	%A	%C	%H
2	251.7	58.6	70.8	35.7	41.3
3	278.4	67.0	72.2	36.4	32.9
4	320.4	74.4	76.2	37.8	25.6
5	303.1	66.5	75.1	31.4	34.5
6	270.6	65.7	73.0	36.2	34.3

[AOH] = 1.0 g dm^{-3}; [NVF] = 16 × 10^{-2} mol dm^{-3}; Time = 120 min; [TU] = 2.8 × 10^{-3} mol dm^{-3}; [PMS] = 10 × 10^{-3} mol dm^{-3}; Temp. = 40°C.

Table II and found that grafting ratio, add on, and efficiency increase due to protonation of TU[37] which takes place on increasing the hydrogen ion concentration up to 4.0 × 10^{-3} mol dm^{-3}, which in turn protonated species reacts with PMS to give more primary free radicals. But on further increasing the concentration of [H$^+$] ions beyond 4.0 × 10^{-3} mol dm^{-3}, the grafting parameters decrease while homopolymer increases. It could be explained by following reasons

1. It is due to premature termination of NVF radicals giving rise to the formation of homopolymer.
2. On increasing the hydrogen ion concentration, formation of H$_2$SO$_5$ species increases due to which concentration of HSO$_5^-$ decreases resulting in production of less free radical, thereby decreasing the grafting parameters.

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

Effect of [*N*-vinylformamide]

The effect of concentration of NVF on grafting parameters has been investigated by varying the concentration of NVF from 8.0 × 10^{-2} to 24.0 × 10^{-2} mol dm^{-3} and results are presented in Figure 4. It has been observed that grafting ratio, add on, and efficiency increase on increasing the concentration up to 16 × 10^{-2} mol dm^{-3} and thereafter, grafting parameters decrease. This behavior is attributed to the 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 macroradicals resulting in chain initiation and thereafter themselves become free radical donors to the neighboring molecule leading lower of termination. But on further increasing the concentration of NVF from 16 × 10^{-2} to 24 × 10^{-2} mol dm^{-3}, the results for these grafting parameters are found to be decreased due to the increased viscosity of the reaction mixture which facilitates the formation of homopolymer.
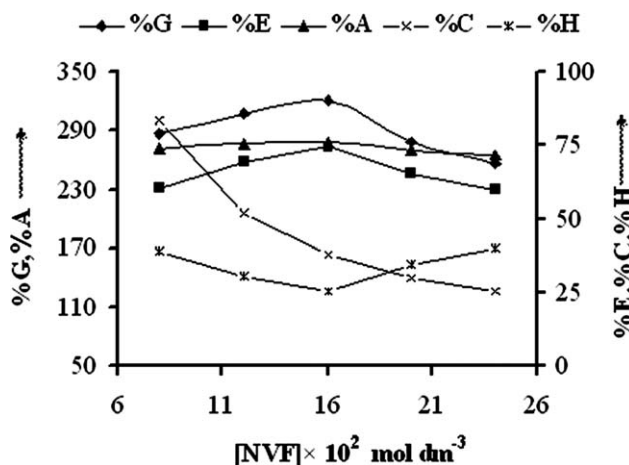
Figure 4 Effect of [*N*-vinylformamide]. [AOH] = 1.0 g dm^{-3}; [PMS] = 10 × 10^{-3} mol dm^{-3}; Time = 120 min; [TU] = 2.8 × 10^{-3} mol dm^{-3}; [H$^+$] = 4 × 10^{-3} mol dm^{-3}; Temp. = 40°C.

Figure 5 Effect of time. [AOH] = 1.0 g dm^{-3}; [PMS] = 10 × 10^{-3} mol dm^{-3}; [NVF] = 16 × 10^{-2} mol dm^{-3}; [TU] = 2.8 × 10^{-3} mol dm^{-3}; [H$^+$] = 4 × 10^{-3} mol dm^{-3}; Temp. = 40°C.

Effect of temperature

The results, for grafting parameters at different temperatures between 30 and 50°C, are summarized in Table III. The grafting parameters increase up to 40°C and thereafter decrease to some extent with further increase in temperature. The increment in grafting parameters in beginning up to 40°C is attributed due to the increase in the formation of active sites on account of enhanced production of primary free radicals with increase in temperature.

The decrement in grafting parameters could be explained as follows:

1. It may be due to the premature termination of growing grafted chains by excess free radicals at higher temperature.
2. Beyond the optimum value increase in temperature may lead to the decomposition of PMS in to HSO$_4^-$, H$_2$O, O$_2$. Since O$_2$ acts as a scavenger for free radicals, which reacts with primary free radicals thereby lowering the free radical concentration.

TABLE III
Effect of Temperature

Temperature (°C)	%G	%E	%A	%C	%H
30	297.0	65.2	74.8	40.0	37.7
35	303.0	69.0	75.1	39.5	30.9
40	320.4	74.4	76.2	37.8	25.5
45	313.0	68.0	75.7	40.5	31.9
50	243.1	58.3	70.8	38.5	41.7

[AOH] = 1.0 g dm^{-3}; [PMS] = 10 × 10^{-3} mol dm^{-3}; [NVF] = 16 × 10^{-2} mol dm^{-3}; [TU] = 2.8 × 10^{-3} mol dm^{-3}; [H$^+$] = 4 × 10^{-3} mol dm^{-3}; Time = 120 min.

Effect of time

To investigate the effect of time on graft copolymerization, the reaction has been carried out by varying the duration of reaction from 60 to 180 min. The results are given in Figure 5. It has been found that grafting ratio; add, on and efficiency increase from 60 to 120 min and thereafter, these parameters decrease. This is attributed to the propagation of grafting chains which takes place due to availability of more active species, which accounts for higher grafting. On further increasing the time interval beyond 120 min, all the active sites get exhausted as the mutual annihilation of growing grafted chains occurs, so that grafting parameters decrease.

Evidence of grafting

Infra-red spectrum of AOH showed strong peaks at 3452.3 cm^{-1} due to ─OH stretching vibrations.[38] On comparing the IR spectra of AOH and alginic acid-*g*-*N*-vinylformamide (presented graph in Figure 6), graft copolymer (alginic acid-*g*-*N*-vinylformamide) showed variations in intensity of ─OH stretching and shifting of the peak appeared due to ─OH stretching from 3452.3 cm^{-1} to 3431.9 cm^{-1} indicating the participation of hydroxyl groups in chemical reaction. In addition to this, the grafting of NVF is further confirmed by characteristic absorption band at 3675.6 cm^{-1} due to appearance ─NH stretching vibration (Amide II) which results from the interaction between ─NH bending vibration and ─CN stretching vibration respectively. A band at 1115.1 cm^{-1} is due ─CN stretching vibration of secondary amide present in pendant chain of poly(*N*-vinylformamide). The appearance of additional new bands due the pendant chain of poly(*N*-vinylformamide) attached in graft copolymer and
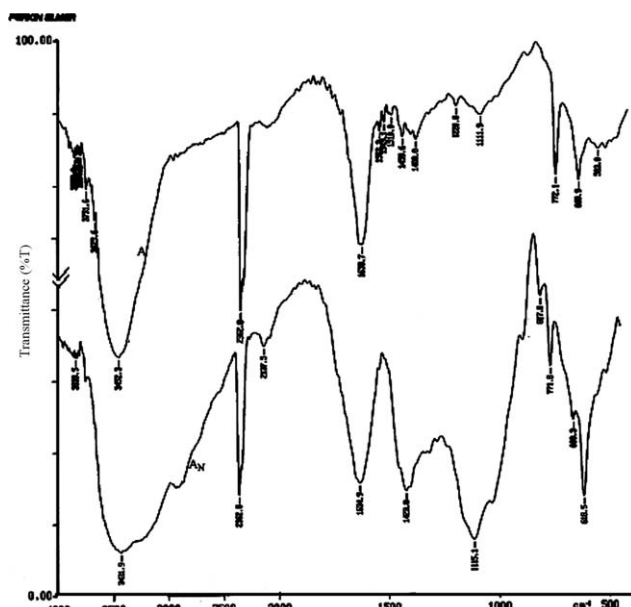
Figure 6 IR spectrum of alginic acid (A) and alginic acid-*N*-vinylformamide (A$_N$).

also the disappearance of OH bending vibration appeared at 669.0 cm^{-1} in AOH showed that grafting have been taken place on —OH of AOH backbone.

Thermogravimetric analysis

Thermogravimetric results are obtained from Figure 7 presented for TGA/DTG curves. The polymer decomposition temperature has been found at 200.0°C. 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
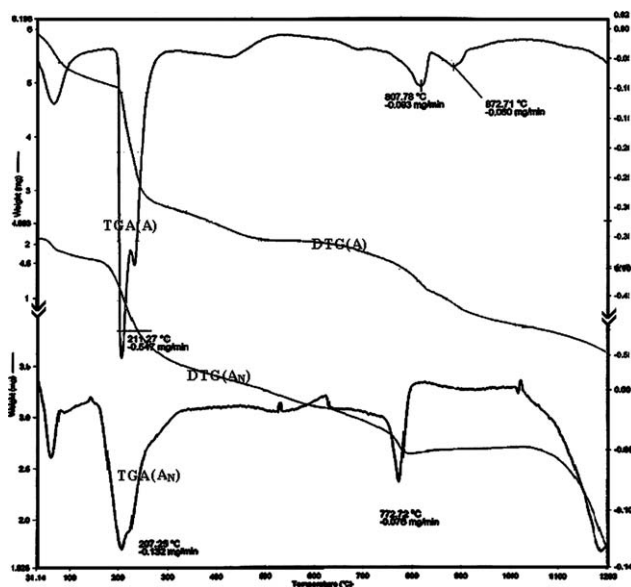

Figure 7 Thermogravimetric trace of alginic acid (A) and alginic acid-*N*-vinylformamide (A$_N$).

TABLE IV
Swelling Capacity of Alginic Acid-*g*-N-vinylformamide

Sample code	[NVF]×10^2 mol dm^{-3}	%G	P_S	S_r
A$_{N1}$	8	287.0	210	2.1
A$_{N2}$	12	307.3	300	3.0
A$_{N3}$	16	320.4	400	4.0
A$_{N4}$	20	279.7	280	2.8
A$_{N5}$	24	257.1	180	1.8

[AOH] = 1.0 g dm^{-3}; [PMS] = 10 × 10^{-3} mol dm^{-3}, [TU]= 2.8 × 10^{-3} mol dm^{-3}; [NVF] = 16 × 10^{-2} mol dm^{-3}; [H$^+$] = 4 × 10^{-3} mol dm^{-3}; Time = 120 min; Temp. = 40°C.

about 252.8°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 alginate and its graft copolymers has also been determined by calculating integral procedural decomposition temperature values using Doyle's equation.[39] The integral procedural decomposition temperature is found to be 267.3°C. Thermogravimetric analysis of alginate shows three steps degradations. First $T_{\max}$, temperature at which maximum degradation occurred, is 211.3°C might be due breaking of segments of D-mannuronic acid and L-glucuronic acid. Second and third $T_{\max}$, 807.8°C and 872.7°C, might be due to elimination of H$_2$O and CO$_2$ respectively. The final decomposition temperature (FDT) has been found at 900.0°C. But in case of alginic acid-*g*-N-vinylformamide, the weight loss 0.5% at about 70.0°C might be due to absorbed water. It has been found that degradation of alginic acid-*g*-N-vinylformamide starts at about 106.3°C temperature. The polymer decomposition temperature has been found at 113.0°C. The rates of weight loss increase with increase in temperature from 170.0°C to 300.0°C, and thereafter decrease and attain a maximum value at about 580.0°C. The degradation of graft copolymer has been taken place in two steps i.e., between 200.0°C to 218.0°C and 750.0°C to 780.0°C temperature ranges. Two $T_{\max}$, temperatures at which maximum degradation occurs, have been found at 207.3°C and 772.7°C, respectively. First $T_{\max}$, at 207.3°C might due to loss of —CO group from pendant chain attached to the polymeric backbone, which is also confirmed by endothermic peak present in DTA curve of alginic acid-*g*-N-vinylformamide at nearly 240.0. The second $T_{\max}$ might be due to the elimination of functional —NH2 group from pendant chain attached to AOH backbone, which is confirmed by endothermic peak present in DTA curve of graft copolymer at 772.1°C. The FDT and integral procedural decomposition temperature have been found at 1100.0°C and 327.9°C,
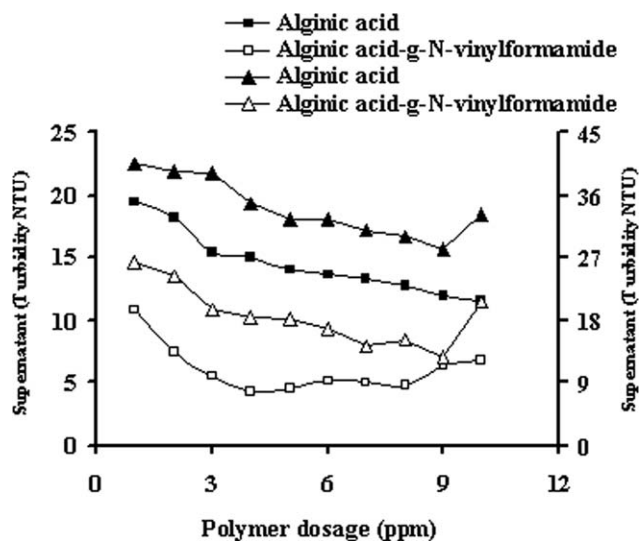
Figure 8 Effect of polymer dosage on turbidity for coking coal (□) and noncoking coal (Δ).

respectively. The two steps degradation and high values of FDT favor the thermal stability of graft copolymer in comparison to the backbone.

Swelling test

As results were summarized in Table IV, a marked increase in value of swelling parameters is observed when graft copolymer samples, prepared at different concentrations of NVF from 8×10^{-2} to 24×10^{-2} mol dm^{-3}, are exposed in water. On increasing the concentration of NVF from 8×10^{-2} to 16×10^{-2} mol dm^{-3} the value of grafting ratio increases, which is due to attachment of longer pendant chains of NVF. The long pendant chains of NVF are responsible for maximum hydrophilic character in graft copolymer thereby increasing the value of swelling ratio. Beyond cited range of NVF concentration, the value of grafting ratio deceases with hydrophilic character due to shorter pendant chains of NVF attached to the polymeric backbone of AOH. It is also observed that the sample of all graft copolymer become swellable up to same time for AOH which become soluble.

Flocculating test

Plots of supernatant turbidity versus polymer dosage for coking and noncoking coals are given in (Fig. 8). It has been found that grafted copolymer (alginic acid-g-N-vinylformamide) having a comb like structure gives better performance by showing lower turbidity than AOH itself. This phenomenon could be explained by considering bridging mechanism.[40–42] The flocculation mechanism can act alone or in combination, depending on the properties of

particles and polymer in solution. In grafted copolymer, the dangling of poly(N-vinylformamide) chains have better approachability[43] to the contaminant coal particles hence increases its flocculation capability.[44] The graft copolymers become highly positively charged species in noncoking coal suspension and interact higher negative charge density coal particles in a greater extent than coking.[45,46] Thus, by grafting of poly(N-vinylformamide) onto AOH, efficient flocculants have been obtained and it could be used for the treatment of coal waste water.

CONCLUSIONS

The thermal data show that the synthesized graft copolymer is thermally more stable than pure AOH. The synthesized graft copolymer i.e., alginic acid-g-N-vinylformamide shows better results for swelling and flocculating properties in comparison to AOH, thus could be interpreted that graft copolymer shows the enhancement in these properties. The spectroscopic data confirm that the grafting of NVF might have taken place at hydroxyl group, which is also supported by a tentative mechanism suggested for grafting. The thermal analysis data show that graft copolymer, a hybrid material in which properties of monomer is added by grafting, could be exploited very well industrially.

References

1. Ravi Kumar, M. N. V. React Funct Polym 2000, 46, 1.
2. Nishio, Y. In New Development of Bio-Based Materials; Kimura, Y., Ohara, H., Eds.; CMC Publication, 2007; pp 132–141.
3. Tripathy, J.; Mishra, D. K.; Srivastava, A.; Mishra, M. M.; Behari, K. Carbohydr Polym 2008, 72, 462.
4. Mishra, D. K.; Tripathy, J.; Mishra, M. M.; Behari, K. J Appl Polym Sci 2008, 110, 3455.
5. Medlin, L. K.; Kooistra, W. H. C. F.; Potter, D.; Saunders, G. W.; Andersen, R. A. Plant Syst Evol (Suppl) 1997, 11, 187.
6. Lim, B. L. A. K.; Kawai, H.; Hori, H.; Osawa, S. Idengaku Zasshi 1986, 61, 169.
7. Rinaudo, M. In Comprehensive Glycoscience; Kamerling, J. P., Ed.; Elsevier: Amsterdam, 2007; Vol. 4, pp 691–735.
8. Santacruz, I.; Gutiérrez, C. A.; Nieto, M. I.; Moreno, R. Mater Res Bull 2002, 37, 671.
9. Painter, T. J. In The Polysacharides; Aspinall, G. O., Ed.; Academic Press: New York, 1983; Vol. 2, pp 195–285.
10. Renken, A.; Hunkeler, D. J Microencapsul 2007, 24, 323.
11. Badwan, A. A.; Abumalooh, A.; Sallam, E.; Abuhalaf, A.; Jawan, O. Drug Dev Ind Pharm 1985, 11, 239.
12. Yoshioka, T.; Tsuru, K.; Hayakawa, S.; Osaka, A. Biomaterials 2003, 24, 2889.
13. Lohmann, D. D. Biodegradable Polymers and Additives in Agricultural Controlled Release Systems, In Proceedings of the 19th International Symposium on Controlled Release of Bioactive Materials; Kopecek, J., Ed.; Controlled Release Society: Deerfield, IL, 1992; p 170.
14. Tsuji, K. In Handbook of Biodegradable Plastics; Dohi, Y., Ed.; MTS: Tokyo, 1995; pp 556–566.
15. Martinsen, A.; Skjak-Braek, G.; Smidsrod, O. Biotechnol Bioeng 1989, 33, 79.

16. Draget, K. I.; Oestgaard, K.; Smidsrod, O. Appl Microbiol Biotechnol 1989, 31, 79.
17. Rhim, J. Lebensm Wiss Technol 2004, 37, 323.
18. Zhang, J.; Xu, S.; Zhang, S.; Du, Z. Iran Polym J 2008, 17, 899.
19. Davidson, I. W.; Sutherland, I. W.; Lawson, C. J. J Gen Microbiol 1977, 98, 603.
20. Jain, S.; Ohman, D. E. In Pseudomonas. Vol. 3: Biosynthesis of Macromolecules and Molecular Metabolism; Ramos, J. L., Ed.; Kluwer Academic: New York, 2004; pp 53–81.
21. Sand, A.; Mishra, D. K.; Yadav, M.; Behari, K. P036. In National Seminar on Polymer Science Technology-Vision and Scenario, Lawn, Auditorium, Faculty of Engineering and Technology, JMI Delhi, December 3, 2008.
22. Yadav, M.; Mishra, D. K.; Sand, A.; Behari, K. P072. In National Seminar on Polymer Science and Technology-Vision and Scenario, Lawn, Auditorium, Faculty of Engineering and Technology, JMI Delhi, December 3, 2008.
23. Kroner, M.; Dupuis, J.; Winter, M. J Prakt Chem 2000, 342, 115.
24. Pinschmidt, R. K.; Wasowski, L. A., Jr.; Orphanides, G. G.; Yacoub, K. Prog Org Coat 1996, 27, 209.
25. Linhart, F.; Degen, H.; Auhorn, W.; Kroener, M.; Hartmann, H.; Heide, W. U. S. Pat. 4,772,359 (1988).
26. Kroener, M.; Schmidt, W.; Proll, T.; Hartmann, H. U. S. Pat. 4,814,505 (1989).
27. Marhefka, J. N.; Marascalco, P. J.; Chapman, T. M.; Russell, A. J.; Kameneva, M. V. Biomacromolecules 2006, 7, 1597.
28. Senden, R. J.; De Jean, P.; Mc Auley, K. B.; Schreiner, L. J Phys Med Biol 2006, 51, 3301.
29. Wang, L. Q.; Tu, K.; Li, Y.; Zhang, J.; Jiang, L.; Zhang, Z. React Funct Polym 2002, 53, 19.
30. Fanta, G. F. In Block and Graft Copolymerization; Ceresa, R. J., Ed.; Wiley: New York, 1973; pp 1–27.
31. Fanta, G. F. In Block and Graft Copolymerization; Ceresa, R. J., Ed.; Wiley: New York, 1973; pp 29–45.
32. Abd El-Rehim, H. A.; Hegazy El-Sayed, A.; Ali, A. M. J Appl Polym Sci 2000, 76, 125.
33. Nasef, M. M.; Saidi, H.; Nor, H. M.; Foo, O. M. J Appl Polym Sci 2000, 76, 1.
34. Mishra, D. K.; Tripathy, J. Carbohydr Polym 2008, 71, 524.
35. Tripathy, J.; Mishra, D. K.; Yadav, M.; Behari, K. Carbohydr Polym 2010, 79, 40.
36. Mishra, D. K.; Tripathy, J. Carbohydr Polym 2008, 74, 632.
37. Tripathy, J.; Mishra, D. K.; Behari, K. Carbohydr Polym 2009, 75, 604.
38. Sand, A.; Yadav, M.; Mishra, D. K.; Behari, K. Carbohydr Polym 2010, 80, 1147.
39. Doyle, C. D. Anal Chem 1961, 33, 77.
40. Deshmukh, S. R.; Singh, R. P.; Chaturvedi, P. N. J Appl Polym Sci 1985, 30, 4013.
41. Gregory, J. In Polymer Flocculation in Flowing Dispersions; Tadros, T. F., Ed.; London Academic Press, 1982.
42. Bolto, B.; Gregory, J. Water Res 2007, 41, 2301.
43. Bratby, J. Coagulation and Flocculation; Uplands Press Ltd: Croydon; UK, 1980.
44. Erciyes, A. T.; Erim, M.; Hazer, B.; Yagci, Y. Angew Makromol Chem 1992, 200, 163.
45. Singh, R. P.; Jain, S. K.; Lan, N. In Polymer Science Contemporary Themes; Shivaram, S., Ed.; Tata McGraw-Hill: New Delhi, 1991; p 716.
46. Singh, R. P.; Tripathy, T.; Karmakar, G. P.; Rath, S. K.; Karmakar, N. C.; Pandey, S. R.; Kannan, K.; Jain S. K.; Lan, N. T. Curr Sci 2000, 78, 798.