Microwave-Initiated Synthesis of Polyacrylamide Grafted Sodium Alginate: Synthesis and Characterization

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ABSTRACT: Microwave-initiated synthesis of polyacrylamide-grafted sodium alginate, a graft copolymer with wide variety of applications has been reported in this study. The effect of reaction parameters (i.e., irradiation time and monomer concentration) onto the percentage grafting has been investigated. The resulting polymer has been characterized by a variety of characterization techniques such as intrinsic viscosity measurement, Fourier transform infrared spectra, ¹³C NMR spectra, elemental analysis, thermogravimetric analysis, molecular weight determination using static light scattering analysis, and scanning electron micrographs. Further, the flocculation efficiency of this graft copolymer has been investigated in coal suspension. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 63–71, 2010

Key words: FTIR; graft copolymers; light scattering; NMR; polysaccharides

INTRODUCTION

Graft copolymerization is a technique for modifying the chemical and physical properties of natural and synthetic polymers. Applications of these modification reactions are useful in the field of polymer science. Chemical grafting is one of the most effective method for modifying structure and properties of biopolymers. Graft copolymerization of natural polysaccharides is becoming an important resource for developing advanced materials as it can improve the functional properties of natural polysaccharides.¹⁻¹⁰ The grafted polymers are usually synthesized by conventional redox grafting method^{11–16} by micro-wave irradiation,^{7,8} gamma-ray irradiation,^{17,18} or using electron beam.¹⁹ Among these methods, microwave irradiation exhibits the most potential to synthesize the grafted polymers, because as the free radicals are generated by means of microwave photons (not by free-radical initiators), steric hindrance is completely ineffective here, leading to a much higher percentage grafting as compared with the conventional method of synthesis. Moreover, in microwave irradiation-based synthesis, the percentage grafting depends on the reaction parameters, i.e. monomer concentration, power, and irradiation

time; the last two factors are electronically controlled, thus ensuring high reproducibility. Further, microwave irradiation as efficient thermal energy constitutes a very original method of heating materials, different from the classical ones. Main advantage is that, it results in almost instantaneous homogeneous heating of materials in a selective manner.^{20–25} In addition, because no initiator is used here, the process conforms to the ideology of green chemistry. As a tailor-made material, grafted polymers find numerous applications as matrix for controlled drug release,^{2,26–28} gums with improvised properties,¹ flocculants,^{11–16} etc. Further, these graft copolymers open the possibility of recycling the wasted polysaccharides from various industrial processes towards useful grafted products.²⁹

Global environment concerns and sustainable ecofriendly approach in the development of materials for high technology have directed to generate better flocculants based on modified polysaccharides for wastewater treatment.

Wastewater contains solid particles with a wide variety of shapes, sizes, densities, etc. Specific properties of these particles affect their behavior in liquid phases and thus the removal capabilities. Many chemical and microbiological contaminants found in wastewater get adsorbed in these solid particles. Thus, an essential step for purification and recycling of wastewaters and industrial effluents is removal of these solid particles. Flocculation is a technique where polymers are involved in a solid–liquid separation by aggregation process of colloidal particles.^{30,31}

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Figure 1 Structure of SAG.

Polysaccharides are inexpensive, abundant, and available from plant, forest, and microbial resources, biodegradable and shear stable; however, poorly efficient as flocculant at low doses. On the other polyacrylamide (PAM)-based flocculants hand, mostly used in wastewater and industrial effluent treatments are highly efficient at very low doses, fragile, and inexpensive. However, they are nonbiodegradable and not shear resistant. By combining the properties of both, one can get a superior polymeric flocculant, which is synergistically efficient at low doses, controlled biodegradable, shear resistant, inexpensive, and ecofriendly. In addition, PAMbased flocculants are entirely petroleum-based products. By grafting PAM with polysaccharide, one can be able to partly compensate the dependence on petroleum as a raw material.

An important water soluble polysaccharide is sodium alginate (SAG). It is the sodium salt of alginic acid (its empirical chemical formula is NaC₆H₇O₆) (Fig. 1), which is a linear unbranched polymer containing $\beta - (1 \rightarrow 4)$ -linked D-mannuronic acid (M) and α -(1 \rightarrow 4)- linked L-guluronic acid (G) residues. It is extracted from the cell wall of brown algae. It is extensively used by the food industries to increase viscosity and as an emulsifier. It is also used in indigestion tablets and in preparation of dental impressions. Another major use of SAG is reactive dye printing, where it is used in the textile industry.

This study deals with the synthesis of various grades of graft copolymers based on acrylamide and SAG via microwave irradiation, effect of reaction parameters onto the percentage grafting and their physicochemical characterization. Moreover, the applicability of these graft copolymers as polymeric flocculants has been investigated in synthetic colloidal suspension (coal fine suspension).

EXPERIMENTAL

Materials

SAG was a gift sample from Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana, India. Acrylamide was procured from E. Merck, Germany. Ceric ammonium nitrate was purchased from Loba Chemie, Mumbai, India. Analar grade of acetone and hydroquinone (HQ) was supplied by S. D. Fine Chemicals, Mumbai, India. All the chemicals were used as received, without further purification.

Coal sample was collected from R-7 seam of Jhanjra colliery, Eastern Coalfields Limited, India.

Synthesis

Synthesis of the graft copolymer by "microwave initiated" method (SAG-g-PAM)

In this method, microwave irradiation was used to generate the free-radical sites on the polysaccharide backbone. The details of the method of synthesis used were as follows:

One gram of SAG was dissolved in 40 mL distilled water. Desired amount of acrylamide was dissolved in 10 mL water and was added to the SAG solution. They were mixed well and was transferred to the reaction vessel (1000 mL Scott-Duran beaker) which was then placed on the turntable of a microwave oven ("20 Liters" LG Microwave oven Model: MG-3937 C). A temperature probe was also incorporated. Now, microwave irradiation at 900 W of power was performed for desired amount of time ranging from 1 to 4 min. Periodically, the microwave irradiation was paused and the reaction mixture was cooled by placing the reaction vessel in cold water (the temperature of the reaction mixture was not allowed to exceed 70°C, to avoid damage to the

Grafting of acrylamide onto the backbone of sodium alginate Initiation:

SAGOH + M <u>MW</u> ► SAGO^{*} + M^{*}

Propagation:

- SAGO M* $SAGO^{*} + M$ SAGOMM SAGO M* + M SAGOMM^{*} n-1 + M SAGOM, Termination: SAGOM_n^{*} + SAGOM_n^{*} --> Graft copolymer **Competing side reaction** Formation of homopolymer Μ MM M_n' SAGO^{*} + M_nH (Homopolymer) M_n SAGOH

SAGOH- Sodium Alginate

M - Monomer (acrylamide)

MW - Microwave photon

Scheme 1 Schematic representation for the synthesis of SAG-*g*-PAM from SAG using microwave irradiation.

Synthetic Details of SAG-g-PAM											
Microwave initiated synthesis (using 900 W microwave radiation)											
Polymer grade	Amount of SAG ^a (mole)	Amount of Acrylamide (mole)	Time (min)	Intrinsic Viscosity (dL/g)	% Grafting ^b	Wt Average Mol. Wt (g/mol)					
SAG-g-PAM 1	0.0062	0.14	1	10.2	11	2.15×10^{4}					
SAG-g-PAM 2	0.0062	0.14	2	10.9	22	2.75×10^4					
SAG-g-PAM 3	0.0062	0.14	3	11.0	25	$2.98 imes 10^4$					
SAG-g-PAM 4	0.0062	0.14	4	10.8	21	2.62×10^4					
SAG-g-PAM 5	0.0062	0.17	3	11.2	30	3.40×10^4					
SAG-g-PAM 6	0.0062	0.21	3	11.6	37	$\textbf{4.30}\times\textbf{10}^{4}$					
SAG-g-PAM 7	0.0062	0.25	3	11.5	36	4.01×10^4					
C		Sodium	Alginate (SA	G)							
SAG	_	-	_	9.5	0	1.94×10^4					

TABLE I Synthetic Details of SAG-g-PAN

^a Calculated based on anhydroglucose unit (AGU). 1 mole of AGU = 162 g.

^b % grafting = $\frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{100.} \times 100.$

g = _______wt. of polysaccharide

polymer backbone and to avoid excessive formation of hazardous reaction vapors).

Once the microwave irradiation for the intended period of time was complete, the reaction vessel and its contents were finally cooled and kept undisturbed for 24 h to complete the grafting reactions. The reaction was terminated by the addition of saturated solution of HQ. Now, the gel-like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of grafted polymer was collected and dried in hot air oven. Subsequently, it was pulverized and sieved. Scheme 1 gives the proposed mechanism for the synthesis of graft copolymer using microwave irradiation. The synthesis parameters are summarized in Table I.



Figure 2 Effect of irradiation time onto percentage grafting (keeping other factors constant).

Various grades of SAG-*g*-PAM have been developed by varying the reaction parameters. Effect of irradiation time onto percentage grafting and effect of monomer concentration onto percentage grafting has been depicted in Figures 2 and 3, respectively.

Purification of the graft copolymer by solvent extraction method

Any occluded PAM formed by competing homopolymer formation reaction was removed from the grafted polymers by solvent extraction using a mixture of formamide and acetic acid (1 : 1 by volume).³²



Figure 3 Effect of monomer concentration onto percentage grafting (keeping other factors constant).

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Elemental Analysis Result									
Polymer	% C	% H	% N	% O					
SAG	36.5	4.0	0.4	47.1					
PAM	50.8	7.7	19.8	21.7					

5.1

7.5

40.5

TABLE II Elemental Analysis Result

Characterization

SAG-g-PAM 6

Intrinsic viscosity measurement

41.0

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer at 25°C. The viscosities were measured in 1M NaNO₃ solution. The pH of the solution was neutral. The time of flow for solutions was measured at four different concentrations. From the time of flow of polymer solutions (t) and that of the solvent (t_0 , for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity was calculated from the relation $\eta_{sp} = \eta_{rel} - 1$. Then, the reduced viscosity (η_{sp}/C) and the inherent viscosity $(\ln \eta_{rel}/C)$ were calculated, where C is the polymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots, i.e. η_{sp}/C versus C and ln η_{rel}/C versus C, to zero concentration.³³ The intrinsic viscosity of the SAG and various grades of the graft copolymers have been summarized in Table I.

Determination of weight average molecular weight by static light scattering analysis

The weight average molecular weight (M_w) of SAG and various grades of SAG-*g*-PAM was determined by static light scattering analysis using Light Scattering Spectrophotometer (Model Nano ZS made by Malvern Inst., UK). Their values have been reported in Table I.

Elemental analysis

The elemental analysis of SAG, PAM, and SAG-*g*-PAM 6 was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model - Vario EL III). The estimation of five elements, i.e. carbon, hydrogen, nitrogen, oxygen, and sulphur was undertaken. The results have been summarized in Table II.

Fourier transform infrared spectroscopy

The Fourier transform infrared (FTIR) spectra of SAG [Fig. 4(a)], PAM [Fig. 4(b)], and SAG-*g*-PAM 6 [Fig. 4(c)] were recorded in solid state using KBr pellets with an FTIR spectrophotometer (Model IR-

Prestige 21, Shimadzu Corporation, Japan) between 500 and 4000 cm^{-1} .

¹³C NMR spectroscopy

% S

0.0

0.0

0.0

¹³C NMR spectra of SAG [Fig. 5(a)], acrylamide [Fig. 5(b)], and SAG-*g*-PAM 6 [Fig. 5(c)] were recorded at 400 MHz with a Bruker spectrophotometer.



Figure 4 FTIR spectra of (a) SAG, (b) PAM, and (c) SAG*g*-PAM 6.



Figure 5 ¹³C NMR spectra of (a) SAG, (b) acrylamide, and (c) SAG-*g*-PAM 6.

Thermogravimetric analysis

The thermal analysis of SAG and SAG-*g*-PAM 6 has been carried out with Thermo Gravimetric Analyzer Instrument, (Model – DTG – 60; Make – Shimadzu, Japan). Thermogravimetric analysis (TGA) was performed up to a temperature of 600°C, starting from 25°C in an atmosphere of nitrogen. The heating rate was uniform in all cases at 5°C/min. Figure 6(a,b) illustrates the TGA curve of SAG and SAG-*g*-PAM 6.

Scanning electron microscopy

Surface morphology of SAG, PAM, and best grade of SAG-*g*-PAM (i.e. SAG-*g*-PAM 6) were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan). The SEM micrographs of SAG [Fig. 7(a)], PAM [Fig. 7(b)], and SAG-*g*-PAM 6 [Fig. 7(c)] have been shown.

Investigations on flocculation characteristics

Flocculation tests of coal suspension were carried out by using Flocculator/Jar Test Apparatus (Make: Simeco, Kolkata, India).

A suspension of coal (0.25%; prepared by mixing 1 g in 400 mL of distilled water) was used for flocculation study. The suspension was taken in a 1-L beaker and the flocculant was added in solution form. The following procedure was uniformly applied to all the suspensions. Immediately after the addition of flocculant, the suspension was stirred at a constant speed of 50 rpm for 5 min. The flocs were then allowed to settle down for 15 min. At the end of the settling period, the turbidity of the supernatant liquid was measured. The flocculant dose was varied from 0.25 to 1.5 ppm, calculated with respect to the total weight of the solution. The results are shown in Figure 8.

DISCUSSIONS

Synthesis

Synthesis of SAG-g-PAM by microwave irradiation

SAG-*g*-PAM has been synthesized by using microwave irradiation. Various grades of the grafted polymer were synthesized by varying the reaction parameters (i.e., irradiation time and monomer concentration) as given in Table I. The optimized grade has been determined by its higher percentage grafting and intrinsic viscosity. From Table I, it is evident that the grafting is optimized at monomer concentration of 0.21 moles and at an irradiation time of 3 min, when the microwave power is maintained at 900 W.

When small polar molecules like water are irradiated with microwave, it results in rotation of the molecules, leading to generation of heat. However, no free radical is produced as such.







(a) SAG



(b) PAM



(c) SAG-g-PAM 6

Figure 7 SEM micrographs of (a) SAG, (b) PAM, and (c) SAG-*g*-PAM 6.

However, if bigger molecules or macromolecules are present, rotation of the entire molecule is not possible. In that case, the microwave is absorbed by the polar groups present (i.e., —OH groups attached to SAG backbone) which then behave as if they were anchored to an immobile raft and its immobile localized rotations³⁴ will occur in the MW region and consequently, the severing of bond leading to the formation of free-radical sites.

Further, the microwave energy absorbed by the water molecules is quickly transferred to the acrylamide molecules, causing "dielectric heating" that results in severing of the double bonds; thus, producing another set of free radicals. The free radicals thus created then recombined with each other through initiation, propagation, and termination steps to produce the graft copolymer. The proposed mechanism has been shown in Scheme 1.

A series of seven graft copolymers have been synthesized by microwave irradiation. For the first four graft copolymers (1–4), the exposure time was varied with the concentration of acrylamide and SAG fixed. For the second set of four graft copolymers (3, 5–7),



Figure 8 Jar test result in 0.25 wt % coal suspensions using SAG and various grades of grafted SAG as flocculants.

only acrylamide concentration was varied keeping the other parameters constant.

Effect of irradiation time. It is obvious from Table I as well as from Figure 2 that with increase in irradiation time (1–4 min), the percentage grafting increases up to 3 min (which is optimized) after which it decreases. This may be because of the fact that beyond exposure time of 3 mins; the prolonged exposure of microwave irradiation may have degraded the polysaccharide backbone, thereby decreasing the percentage grafting and intrinsic viscosity.

Effect of monomer concentration. Grafting ratio increased on increasing the monomer concentration from 0.14 to 0.21 moles (Fig. 3). The increase in percentage grafting may be because of the availability of more monomer. But percentage grafting decreased with further increase in monomer concentration beyond 0.21 moles. This may be because of the more homopolymer formation.

Interpretation for using HQ as inhibitor

Inhibitors react with chain radicals to terminate chain propagation and the resulting HQ radical is stable and cannot initiate further polymerization. The stability of the HQ radical is because of the delocalization of electron charge density throughout the aromatic structure, thus addition of HQ quench the grafting reaction. This inhibitor action of HQ is a strong support for the free-radical mechanism.

$$SAGO^* + HQ \longrightarrow SAGOH + HQ^*$$

Characterization

Estimation and interpretation of intrinsic viscosity

The intrinsic viscosity was evaluated for SAG and different grades of SAG-g-PAM, as given in Table I.

As evident, the intrinsic viscosities of all the grades of SAG-*g*-PAM are greater than that of SAG. This can be explained by the higher molecular weight of SAG-*g*-PAM than SAG, due to the grafting of the PAM branches on the main polymer backbone. Intrinsic viscosity is a measure of hydrodynamic volume of a polymer in solution. With increase in molecular weight, the radius of gyration would also increase, which gives higher intrinsic viscosity. The same has been reflected in case of grafted SAG.

Further, it has been observed that a correlation is present between percentage grafting and intrinsic viscosity of the different grades of SAG-*g*-PAM (i.e., higher the percentage grafting, higher is the intrinsic viscosity). This is obvious as a higher percentage grafting translates to higher molecular weight (also indicated in Table I) which in turn leads to higher infrinsic viscosity. Determination of weight average molecular weight by static light scattering technique

As expected, all the grades of SAG-*g*-PAM have higher molecular weight than SAG (Table I). Also, it is evident that higher the percentage grafting, higher is the molecular weight as a consequence of the longer PAM chains.

Further, a correlation between all the three factors (i.e., percentage grafting, intrinsic viscosity, and weight average molecular weight) of Table I is evident and clearly indicates that the PAM has been grafted onto SAG backbone.

Elemental analysis

The results of elemental analysis for SAG, PAM, and the optimized grade of SAG-*g*-PAM (i.e., SAG-*g*-PAM 6 optimized with respect to percentage grafting, molecular weight, intrinsic viscosity as well as flocculation efficacies) has been given in Table II. The percentage of nitrogen in case of grafted product is significantly high, whereas it is negligible in the base polysaccharide. This confirms that the PAM chains have been grafted on the backbone of SAG.

FTIR spectroscopy

From the FTIR spectrum of SAG [Fig. 4(a)], it is being observed that a broad peak at 3450 cm⁻¹ is due to the stretching vibrations of O–H, a small peak at 2935 cm⁻¹ attributed to the C–H stretching vibrations. The bands at 1085 and 1016 cm⁻¹ are assigned to C–O–C stretching vibrations. It is further noted that two strong peaks at 1620 and 1417 cm⁻¹ are attributed to the COO⁻ groups of carboxylate ion (COO⁻).

In the PAM (PAM) spectrum [Fig. 4(b)], the strong absorption band at 3430 cm⁻¹ is attributed to the N—H stretching vibrations of the primary amide. The two bands at 1680 and 1659 cm⁻¹ are due to amide-I ($v_{C=O}$) and -II (v_{NH}), respectively. The bands at 2930 and 1398 cm⁻¹ are for the C—H and C—N stretching vibrations, respectively. Two other bands at 1450 and 1305 cm⁻¹ are attributed to CH₂ scissoring and CH₂ twisting, respectively.

Few differences have been observed in the spectrum of SAG-g-PAM 6 (i.e., optimized grafted SAG) [Fig. 4(c)]. O–H stretching band of hydroxyl group of SAG and N–H stretching band of amide group of PAM overlap with each other and lead to broad band at 3420 cm⁻¹. The appearance of two sharp peaks at 1685 and 1646 cm⁻¹ are attributed to C=O and N–H stretchings, respectively. Further, there is one more additional band present in grafted product at 1395 cm⁻¹, which is assigned to the C–N stretching bands. Thus, the presence of these additional

bands in case of grafted SAG compared with SAG confirms the successful grafting of PAM chains onto the polysaccharide backbone.

¹³C-NMR spectroscopy

It is being observed from the values of ¹³C NMR spectrum of SAG [Fig. 5(a)] that it has three distinct peaks. The absorption peak at $\delta = 176.6$ ppm is for the carboxyl carbon atom of $-\text{COO}^-\text{Na}^+$ group. The absorption peak at $\delta = 75.9$ ppm is for carbon atoms connected by -OH groups (i.e., the carbon atoms in the six-membered ring except anomeric carbon atom). The peak at $\delta = 100.0$ ppm is attributed to the α carbon atom of the oxygen linkage.

Acrylamide [Fig. 5(b)] had three major peaks in the spectrum. The peak at $\delta = 179$ ppm was for the amide carbonyl carbon. Peaks at $\delta = 130$ and $\delta = 133$ ppm were for two sp² hybridized carbon atoms (i.e., CH₂=CH–).

In the ¹³C NMR spectrum of SAG-*g*-PAM 6 [Fig. 5(c)], there are three additional bands present, compared with base polysaccharide (SAG). The peak at $\delta = 38.3$ ppm is for -CH₂-CH₂- groups those have been formed during the polymerization reaction. The presence of a very intense peak at $\delta = 177.6$ ppm due to carbonyl groups, along with two additional peaks because of the methylene group at $\delta = 31.6$ ppm and the carbon connected to carbonyl group at $\delta = 38.3$ ppm confirms that grafting of PAM onto the SAG backbone does take place.

As seen in ¹³C NMR spectrum of the graft copolymer and acrylamide, acrylamide had two peaks at δ = 130 and 133 ppm for two sp² hybridized carbon atoms, which were absent in the graft copolymer. Moreover, two additional peaks are present for graft copolymer at δ = 38.3 and 31.6 ppm, which is for the sp³ hybridized carbon atoms (i.e. $-(CH_2-CH)_n$ units in the graft copolymer). Neither the SAG nor the acrylamide spectrum had this peak. So, the absence of peak at δ = 130 and 133 ppm and the presence of a peak at δ = 38.3 and 31.6 ppm is a clear evidence of the grafted PAM chains onto the backbone of SAG.

Thermogravimetric analysis

The TGA thermograms of SAG and SAG-g-PAM6 were obtained at a scan rate of 5° C/min in nitrogen atmosphere (Fig. 6). In the case of SAG [Fig. 6(a)], two distinct zones are observed where the weight is being lost. The initial weight loss is because of the presence of small amount of moisture present in the polysaccharide. The second degradation zone is because of the decomposition of polymer backbone. In the case of SAG-g-PAM 6 [Fig. 6(b)], apart from the two zones, there is one addition degradation

zone, which is due to the presence of PAM chain grafted onto SAG backbone.

Scanning electron microscopy analysis

It is obvious from the SEM micrographs of SAG and its grafted product (Fig. 7), profound morphological changes have taken place because of grafting of PAM chains on SAG. Thus, it is evident that the original morphology of SAG is lost after grafting.

Flocculation investigations

The flocculation performance of SAG and all the graft copolymers was compared in 0.25 wt % coal suspensions. The result is shown in Figure 8. In this case, the turbidity of the supernatant liquid after flocculation was plotted against the polymer concentration. It is obvious from these results that SAG-*g*-PAM 6, which is having higher percentage grafting and higher molecular weight, is a better flocculant in coal suspension compared with other grades of the grafted polymer and SAG.

CONCLUSION

From the above experimental investigations, it has been observed that various grades of SAG-g-PAM can be synthesized by using only microwave irradiation. The synthesized graft copolymers have been characterized physicochemically by a variety of characterization techniques, confirming that PAM has been grafted onto SAG backbone. Further, the developed material finds potential application as flocculant.

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