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Microwave based synthesis of polymethyl methacrylate grafted sodium alginate: its application as flocculant

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ABSTRACT

Polymethyl methacrylate grafted sodium alginate (SAG-g-PMMA) was synthesized by *microwave assisted method*. The grafting of the PMMA chains on the polysaccharide backbone was confirmed through intrinsic viscosity study, FTIR spectroscopy, elemental analysis (C, H, N, O and Na), SEM and TGA study. The intrinsic viscosity of sodium alginate appreciably improved on grafting of PMMA chains, thus resulting grafted product with potential application as superior viscosifier. Further, flocculation efficacy of the graft copolymer was studied in coal fine suspension through jar test procedure, toward possible application as flocculant.

1. Introduction

1.1. Water scarcity: the impending disaster

Water is one of the key factors required for existence and flourishing of carbon based life form. The abundance of water is the single most important factor that distinguishes this planet from all others of this solar system. The importance of water for existence of life is so important that the search for water in other planets has become synonymous to search for life. However, most of the water on this planet is stored in oceans as saline water and hence is not fit for direct human consumption. The small percentage of freshwater that exists occurs in ice caps and inland water bodies, which are the key to fulfilment of our diverse needs.

In the present scenario, global warming is responsible for rapid disappearance of the ice caps (glaciers) which in turn in the near future will result in volume of water in the all season glacier fed rivers to dwindle. The ever increasing pollution of water bodies is making the scenario worse. Because of these factors, water or rather the shortage of it is emerging as one of the most significant problems of the recent times.

The other fundamental need of human civilization is energy. Coal has been the principal source of industrial energy for much of the developing world. Although, petroleum based fuels are 'greener', the distribution of coal minerals on this planet are more even and hence, the importance of coal in development of world economy cannot be ignored. Washing coking coals with water before their utilization in thermal power plant and cement industry is a general practise and is gaining popularity. Washed coals have higher calorific value and cause lesser air pollution on burning. However, we seem to trade one type of pollution for the other. The very process of washing of coal produces effluent with coal fine suspension. These coal washery effluents have the potential to pollute huge stretch of the receiving water body. Further, once recovered, the fine coal particles of these effluents serve as a precious fuel commodity which otherwise would have gone waste. Thus, it is evident that treatment of coal washery effluent has both ecological as well as economical benefits.

For the removal of suspended solids from the coal washery effluent, flocculation aided by synthetic and semisynthetic flocculants (Pal, Sen, Karmakar, Mal, & Singh, 2008; Sen, Mishra, Usha Rani, Rani, & Prasad, 2012) seems to be a highly effective strategy.

1.2. Sodium alginate (SAG): a promising polysaccharide

Sodium alginate is the principal commercial water-soluble salt of alginic acid. Other commercially available water soluble salts are potassium alginate and ammonium alginate. Water-insoluble compounds that are marketed are calcium alginate and alginic acid. The only commercially important organic derivative is propylene glycol alginate.

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Sodium alginate is sourced from brown green algae (Phaeophyceae) and sea weeds. It binds 200–300-fold weight of water to give gel formation. Sodium alginate is insoluble in cold water. It has many applications in the food industry as thickeners in fruit jellies, marmalades, ice cream, etc. Propylene glycol esters of alginic acids are used as foam stabilizer. Sodium alginate and its derivatives has long been the focus of many scientific studies. Polyacrylamide grafted sodium alginate as a flocculant has been reported in recent times (Sen, Mishra, Jha, & Pal, 2010; Sen, Singh, & Pal, 2010).

1.3. Sodium alginate molecular structure

Alginate is composed of two building blocks of monomeric units, namely R-D-mannuronopyranosyl and L-guluronopyranosyl units. Ratio of D-mannuronic acid and L-guluronic acid and their sequence determines the alginate properties. Monomers occur in blocked sequences (M & G blocks) as shown in Supplementary Fig. 1.

1.4. The concept of graft copolymers

Graft copolymers by definition, consists of a long sequence of one polymer (backbone polymer) with one or more branches (grafts) of another (chemically different) polymer (Gowariker, Viswanathan, & Sreedhar, 1986, Chapter 12; Odian, 2002). The process of graft copolymer synthesis starts with a preformed polymer (polysaccharide in this case). An external agent is used to create free radical sites on this preformed polymer. Once the free radical sites are formed on the polymer backbone (i.e. preformed polymer), the monomer (i.e. vinyl or acrylic compound) can get added up through the chain propagation step, leading to the formation of grafted chains. The various methods of graft copolymer synthesis actually differ in the ways of generation of the free radical sites on this preformed polymer.

The most contemporary technique in graft copolymer synthesis involves the use of microwave radiations to initiate the grafting reactions. Superiority of this technique over others has been well discussed in earlier studies (Mishra & Sen, 2011; Mishra, Mukul, Sen, & Jha, 2011; Mishra, Sen, Rani, & Sinha, 2011; Mishra, Rani, & Sen, 2012; Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011; Pal, Sen, Ghosh, & Singh, 2012; Sen & Pal, 2009a, 2009b; Sen, Kumar, Ghosh, & Pal, 2009; Sen, Mishra, et al., 2010; Sen, Singh, et al., 2010; Sen, Ghosh, Jha, & Pal, 2011; Usha Rani, Mishra, Sen, & Jha, 2012). Microwave radiations cause 'selective excitation' of only the polar bonds, leading to their rupture/cleavage – thus resulting in formation of free radical sites. The 'C—C' backbone of the preformed polymer being relatively non polar, remains unaffected by the microwave radiation, thus the structural integrity of the backbone remains intact, leading to a superior product (Mishra et al., 2012).

Microwave based graft copolymer synthesis is further classified into two types: microwave initiated synthesis (using microwave radiation alone to initiate grafting) and microwave assisted synthesis (using a synergism of microwave radiation and chemical free radical initiator to initiate grafting).

1.5. Plan of investigation

The study described in this paper involve the synthesis of graft chains of polymethyl methacrylate (PMMA) onto the backbone of sodium alginate, thus resulting in formation of polymethyl methacrylate grafted sodium alginate' (SAG-g-PMMA). The synthesis has been carried out by *microwave assisted method*, which involved a synergism of microwave radiations and ceric ammonium nitrate (CAN) to initiate the grafting reaction. The flocculation efficacy of the grafted product has been studied in coal fine effluents toward its application in coal washery effluent treatment.

2. Materials and methods

2.1. Materials

Sodium alginate and methyl methacrylate were supplied by CDH, New Delhi, India. Ceric ammonium nitrate was supplied by E. Merck (India), Mumbai, India. Acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received; without further purification.

2.2. Synthesis of graft copolymer

2.2.1. Microwave assisted synthesis of polymethyl methacrylate grafted sodium alginate (SAG-g-PMMA), using ceric ammonium nitrate (CAN) as free radical initiator

1 g of sodium alginate was dissolved in 40 ml distilled water. Desired amount of methyl methacrylate was added to above solution. They were mixed well and were transferred to the reaction vessel (250 ml borosil beaker) followed by addition of catalytic amount of ceric ammonium nitrate (CAN). The reaction vessel was placed on the turntable of a microwave oven and microwave irradiation at 800 W of power was performed. Periodically, the microwave irradiation was paused just as the reaction mixture starts boiling (~65 °C) and was cooled by placing the reaction vessel in cold water. This was done to keep any probability of competing homo polymer formation reaction to the minimum.

This *microwave irradiation – cooling* cycle was repeated until a gel like mass was left or up to 3 min of irradiation time (if no gelling took place). Subsequently, the reaction vessel and its contents were finally cooled and kept undisturbed to complete the grafting reaction. Later, the gel like mass left in the reaction vessel was poured into excess of acetone. The resulting precipitate of graft copolymer was collected and was dried in hot air oven. Subsequently, it was pulverized, sieved and purified (as explained in Section 2.2.2). The percentage grafting of this microwave assisted synthesized SAG-g-PMMA was evaluated as:

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

The synthesis details of various grades of the graft copolymer have been shown in Table 1.

2.2.2. Purification of the graft copolymer by solvent extraction method

In an attempt to check possibility of any competing homopolymer formation reaction, the whole synthesis process was repeated as above, but in absence of any polysaccharide (sodium alginate). In absence of the polysaccharide, no product is obtained. This implies that the above process either does not involve any parallel homopolymer formation reaction or if even any homopolymer happen to be formed, it cannot be precipitated in acetone.

However as an added precaution, any occluded polymethyl methacrylate (PMMA) formed by competing homo polymer formation reaction was removed from the graft copolymer synthesized as above, by extraction with acetone for 24 h (Kongparakul, Prasassarakich, & Rempel, 2008). The scheme of synthesis of the graft co polymer has been summarized in Scheme 1.

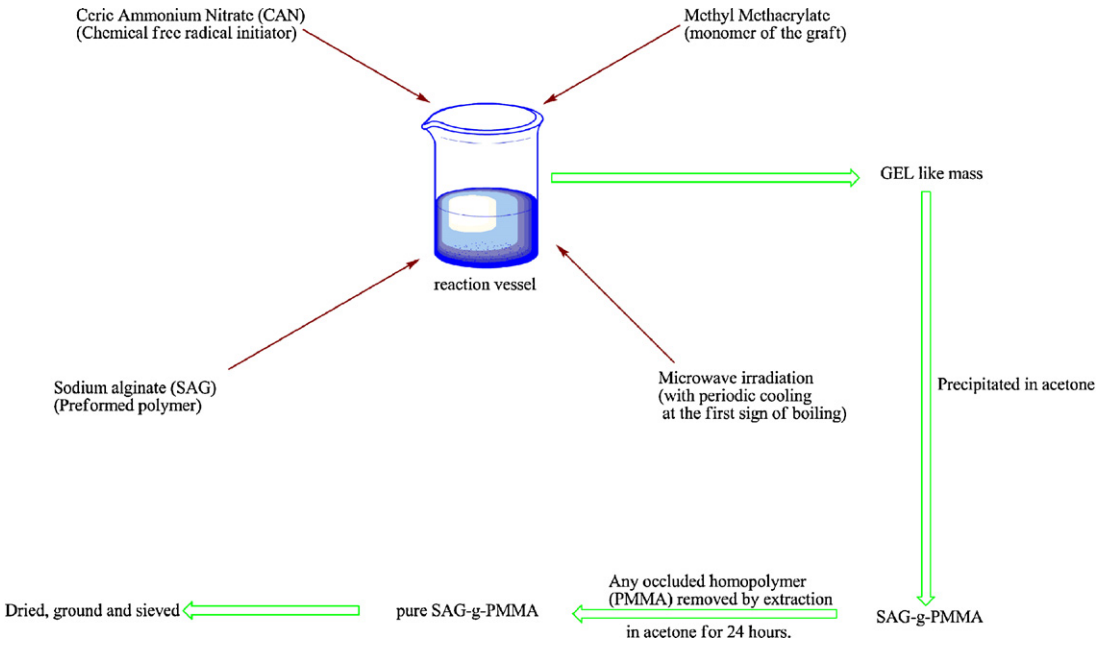
2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelohde viscometer (capillary diameter 0.46 mm)

Table 1
Synthesis details of SAG-g-PMMA.

Grades	Wt. of sodium alginate (g)	Wt. of methyl methacrylate (g)	Wt. of CAN (g)	Time of irradiation (s)	%Grafting	Intrinsic viscosity (dl/g)
SAG-g-PMMA 1	1	5	0.2	50	46	3.2
SAG-g-PMMA 2	1	5	0.3	50	54	3.67
SAG-g-PMMA 3	1	5	0.4	50	77	7.88
SAG-g-PMMA 4	1	10	0.4	50	32	3.08
SAG-g-PMMA 5	1	2.5	0.4	50	18	2.8
SAG-g-PMMA 6	1	7.5	0.4	50	87	8.8
SAG-g-PMMA 7	1	5	0.5	50	36	3.17
SAG (sodium alginate)	–	–	–	–	–	2.79



Scheme 1. Plan of synthesis.

at 25 °C. The viscosities were measured in aqueous solutions. The pH of the solution was neutral. The time of flow for solutions was measured at four different concentrations (0.1%, 0.05%, 0.025% and 0.0125%). 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 (η_{sp}), relative viscosity (η_{rel}) reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) was mathematically calculated as:

$$\eta_{sp} = \eta_{rel} - 1$$
$$\eta_{red} = \frac{\eta_{sp}}{C}$$
$$\eta_{inh} = \frac{\ln \eta_{rel}}{C}$$

where 'C' represents polymer concentration in g/dl.

Subsequently, the reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were plotted against concentration. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots (i.e. η_{red} versus C and $\ln \eta_{inh}$ versus C) to zero concentration (Collins, Bares, & Billmeyer, 1973). The intrinsic viscosity thus evaluated for various grades of the graft copolymer has been reported in Table 1. The relation between intrinsic viscosity and percentage grafting has been graphically depicted in Supplementary Fig. 2.

2.3.2. Elemental analysis

The elemental analysis of sodium alginate (SAG) and that of different grades of SAG-g-PMMA 6 (best grade of the grafted sodium alginate synthesized) was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model – Vario EL III). The estimation of the elements, i.e. carbon, hydrogen, nitrogen, and oxygen were undertaken. Further, sodium content was analyzed by flame photometry (ELICO, model no.: CL378). The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The FTIR spectrums of sodium alginate (Fig. 1(a)) and of SAG-g-PMMA 6 (Fig. 1(b)) were recorded in solid state, by KBr pellet method using a FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000 cm^{-1}.

2.3.4. Scanning electron microscopy

Surface morphology of sodium alginate (Fig. 2(a) and (c)) and SAG-g-PMMA 6 (Fig. 2(b) and (d)) were analyzed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.3.5. TGA studies

The thermo gravimetric analysis (TGA) of sodium alginate and that of the SAG-g-PMMA 6 were carried out with TGA instrument

Table 2
Elemental analysis of SAG and SAG-g-PMMA 6 (best grade).

Polymer grade	%C	%H	%N	%O	%Na
PMMA	59.98	8.05	0.00	31.96	0.00
SAG-g-PMMA 6	34.53	5.962	0.00	54.88	4.628
Sodium alginate	32.34	5.304	0.00	56.85	5.225

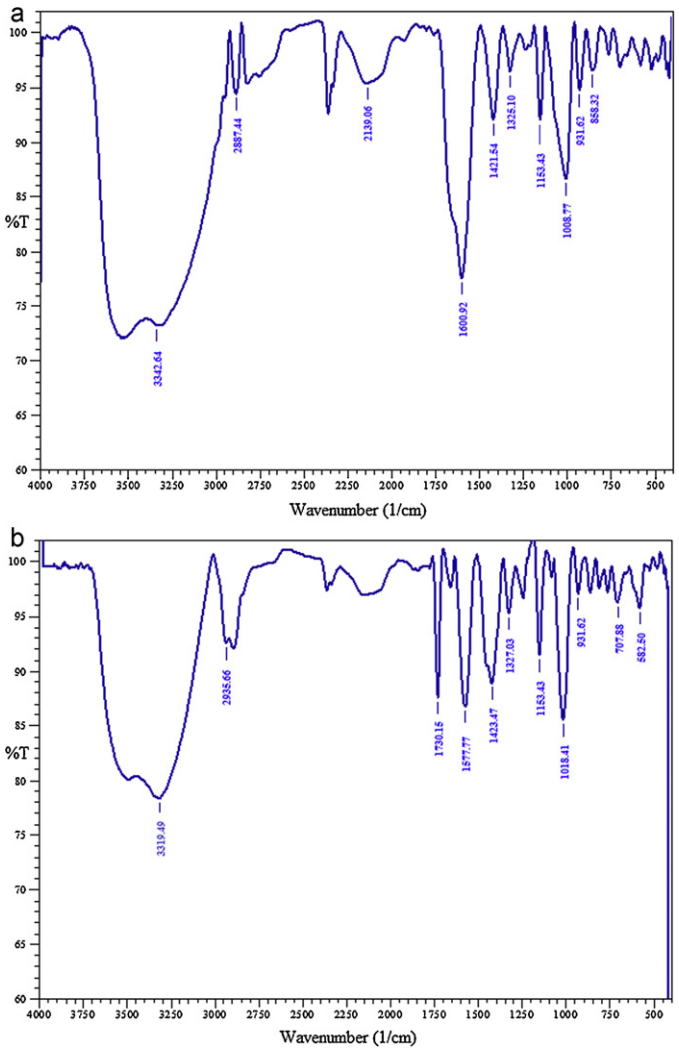


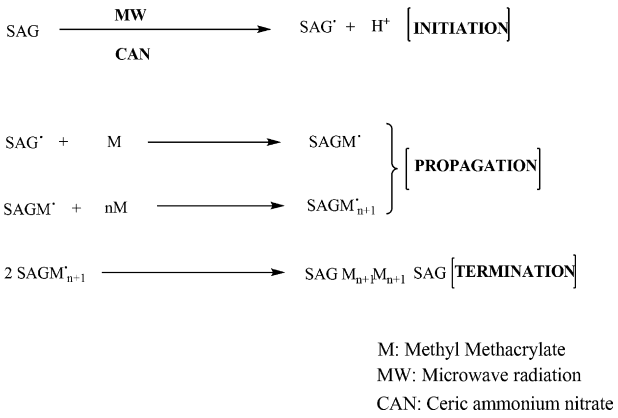
Fig. 1. FTIR spectrum of (a) SAG and (b) SAG-g-PMMA 6.

(Model: DTG-60; Shimzadu, Japan). The study was performed in an inert atmosphere (nitrogen) from 25 °C to 800 °C. The heating rate was uniform in all cases at 5°/min. The concerned TGA curves have shown in Fig. 3(a) and (b).

2.4. Flocculation study in coal fine suspension

Flocculation tests of coal suspensions were carried out by using jar test apparatus. Flocculation efficacy of various synthesized grades of SAG-g-PMMA and that of sodium alginate (starting material) were studied by standard jar test procedure, in 1% coal fine suspension.

All flocculation experiments were carried out in jar test apparatus (Make: Simeco, Kolkata, India). The test protocol involved taking a measured quantity (800 ml) of the 1% coal fine suspension in 1 l borosil beakers. Calculated amount of the flocculant (sodium alginate or various grades of SAG-g-PMMA) or coagulant (alum) was added in concentrated solution form (except in case of blank, where no flocculant/coagulant was added) to achieve the desired dosage (ranging from 0 ppm to 0.625 ppm). The solutions were identically stirred (in jar test apparatus), at 150 rpm for 30 s, 60 rpm for 5 min, followed by 5 min of settling time. Afterwards, supernatant liquid was collected from each jar and optical density was measured in a calibrated spectrophotometer (DR/2400, Hach®) at λ_{max} 520 nm. The flocculation efficacy thus studied for sodium alginate, alum and various grades of SAG-g-PMMA have been graphically compared in Fig. 4(a).



Scheme 2. Mechanism for 'microwave assisted' synthesis of SAG-g-PMMA.

3. Results and discussions

3.1. Synthesis of SAG-g-PMMA by microwave assisted method

SAG-g-PMMA has been synthesized by microwave assisted method. The term *microwave assisted method* has been coined by us in our earlier study (Mishra & Sen, 2011; Mishra, Mukul, et al., 2011; Mishra, Sen, et al., 2011). It refers to a process of graft copolymer synthesis, which is a hybrid of *microwave initiated* and *conventional* method of synthesis i.e. it is based on free radical mechanism using microwave radiation in synergism with chemical free radical initiator (ceric ammonium nitrate) to generate free radical sites on the sodium alginate backbone. Various grades of the graft copolymer were synthesized by varying the ceric ammonium nitrate (CAN) and methyl methacrylate (monomer) concentration. In each case, the microwave irradiation of the reaction mixture was continued until it sets into a viscous gel like mass (or up to 3 min if no gelling took place). The synthesis details have been tabulated in Table 1. The optimized grade has been determined through its higher percentage grafting and intrinsic viscosity (which is proportional to molecular weight). The approach of synthesis involved optimization with respect to CAN, keeping the methyl methacrylate concentration constant (i.e. SAG-g-PMMA 1, SAG-g-PMMA 2, SAG-g-PMMA 3 and SAG-g-PMMA 7); followed by optimization with respect to methyl methacrylate, keeping the CAN concentration as optimized before (i.e. SAG-g-PMMA 3, SAG-g-PMMA 4, SAG-g-PMMA 5, SAG-g-PMMA 6). From Table 1, it is obvious that the grafting is optimized at methyl methacrylate concentration of 7.5 g and CAN concentration of 0.4 g in the reaction mixture (~50 ml), when the microwave power is maintained at 800 W.

CAN is electron deficient molecule. So it takes electrons from alcoholic oxygen in sodium alginate to form a new bond i.e. Ce—O. This bond being more polar (than O—H bond) breaks easily in the presence of microwave irradiation to form free radical site on the backbone of sodium alginate, from where the graft chains grow. The proposed mechanism of microwave assisted synthesis has been hypothesized in detail in our earlier studies (Rani, Sen, Mishra, & Jha, 2012; Mishra, Mukul, et al., 2011; Mishra, Sen, et al., 2011).

The proposed mechanism of microwave assisted grafting has been depicted in Scheme 2.

Mechanisms of conventional, microwave initiated and assisted have been discussed in detail in our earlier studies (Banerjee et al., 2012; Mishra et al., 2012; Rani et al., 2012; Sen et al., 2009).

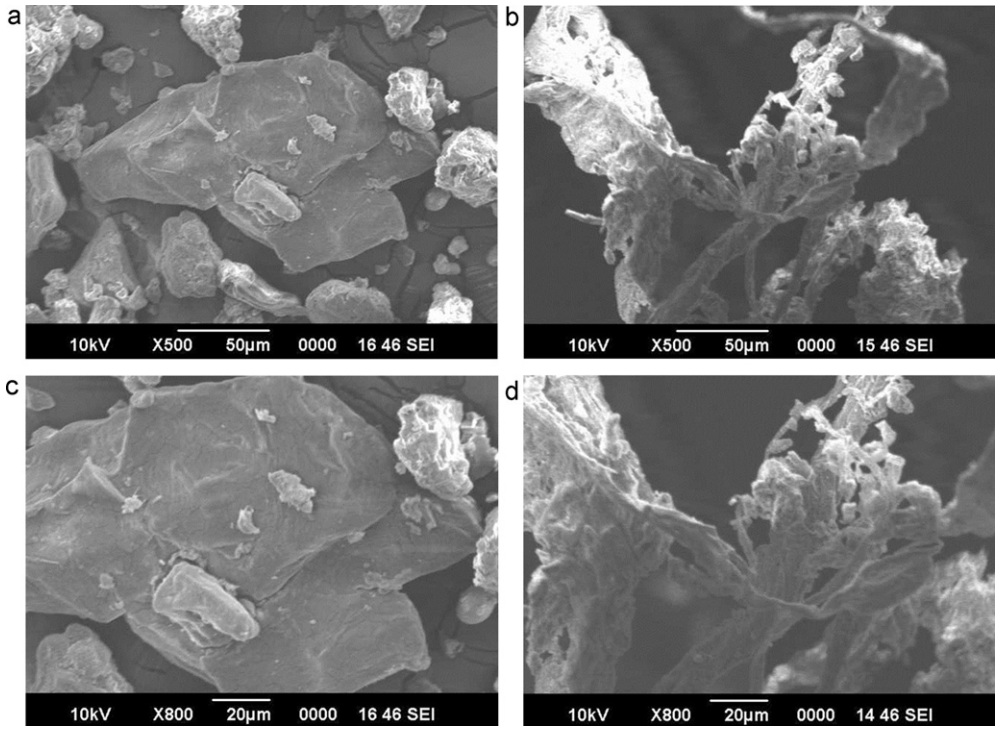


Fig. 2. SEM morphology of (a) SAG (500× magnification), (b) SAG-g-PMMA 6 (500× magnification), (c) SAG (800× magnification) and (d) SAG-g-PMMA 6 (800× magnification).

3.2. Characterization

3.2.1. Estimation and interpretation of intrinsic viscosity

The intrinsic viscosity was evaluated for sodium alginate and for all the synthesized grades of SAG-g-PMMA, as shown in Table 1.

Intrinsic viscosity is practically the hydrodynamic volume of the macromolecule in the solvent (water in this case) solution. As evident from Table 1, intrinsic viscosities of all the grades of SAG-g-PMMA are greater than that of sodium alginate. This is due to the increase in hydrodynamic volume resulting from grafting of the PMMA chains on the main polymer backbone (sodium alginate). The grafted PMMA chains increase hydrodynamic volume by two ways:

(1) by uncoiling of the polysaccharide chain through steric hindrance to intra molecular bonding;
(2) by contributing their own hydrodynamic volume.

Further, the increase in intrinsic viscosity due to grafting is in good agreement with Mark–Houwink–Sakurada relationship (intrinsic viscosity $\eta = KM^{\alpha}$, where K and α are constants, both related to stiffness of the polymer chains), which explains the increase in intrinsic viscosity as a result of increase in molecular weight (M) due to the grafted PMMA chains.

The correlation between percentage grafting (% G) and intrinsic viscosity (η) has been plotted in Supplementary Fig. 2.

Huggins and Kramers equation constants (k' and k'') obtained from the slopes of plots of reduced and inherent viscosity of SAG are 0.041 and 0.399. These values for SAG-g-PMMA6 are −0.560 and 0.916 respectively.

3.2.2. Elemental analysis

The results of elemental analysis for sodium alginate (SAG), poly methyl methacrylate (PMMA) and that of the best grade of poly methyl methacrylate grafted sodium alginate (SAG-g-PMMA 6) are given in Table 2. As evident from the table, the grafted product has a elemental composition that is intermediate of its constituents (SAG and PMMA).

3.2.3. FTIR spectroscopy

As evident from Fig. 1(a), SAG has a O—H stretching peak at 3342.64 cm^{-1}, C—H stretching peak at 2887.44 cm^{-1} and C—O—C stretching peak at 1600.92 cm^{-1}.Two COO^{-} symmetric stretching peaks are evident at 1421.54 and 1325.10 cm^{-1} respectably.

From Fig. 1(b) it is clear that in addition to the above peaks, SAG-g-PMMA6 have an additional peak at 1730.18 cm^{-1}, which is attributed to the stretching vibration of 'C=O' bonds of the grafted PMMA chains. The existence of this peak confirms grafting of PMMA chains onto the backbone of SAG.

The important FTIR peaks of sodium alginate and that of SAG-g-PMMA 6 have been reported in Supplementary Table 1.

3.2.4. Scanning electron microscopy (SEM) analysis

It is evident from the SEM micrographs of sodium alginate (Fig. 2(a) and (c)) and that of the best grade of SAG-g-PMMA 6 (Fig. 2(b) and (d)) that profound morphological change, in form of transition from granular structure to fibrillar structure, have taken place because of grafting of PMMA chains on the polysaccharide.

3.2.5. Thermal analysis

The TGA curves of SAG (Fig. 3(a)) essentially involved three distinct zones of weight loss. The initial weight loss is at 25–110 °C. This is due to the traces of moisture present .The second zone (225–380 °C) is due to degradation of COO^{-} groups and consequent loss of CO_2 (decarboxylation). The third zone of weight loss (380–800 °C) was due to degradation of the SAG backbone (probably due to degradation of C—O—C bonds).

In case of SAG-g-PMMA 6 (Fig. 3(b)), a fourth zone of weight loss (550–800 °C) overlaps the third zone of weight loss of SAG backbone. This fourth zone of weight loss (500–800 °C) is due to degradation of PMMA chains grafted on SAG moiety.

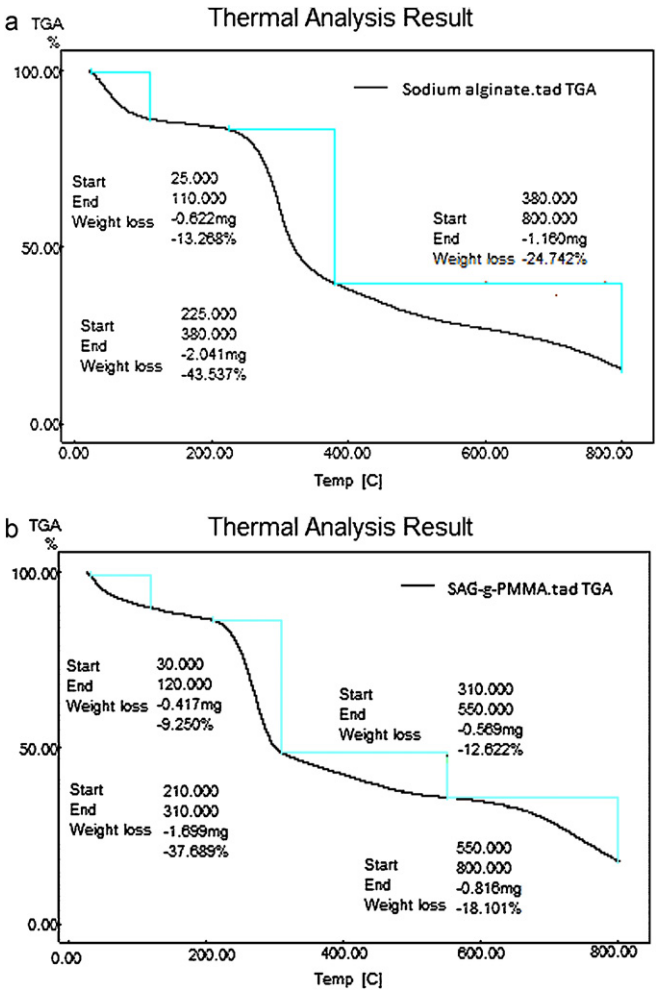


Fig. 3. TGA of (a) SAG and (b) SAG-g-PMMA 6.

3.3. *Flocculation study and dosage optimization in coal fine suspension*

The flocculation study in 1% coal fine suspension in jar test apparatus, for dosage varying between 0 ppm (control) and 0.625 ppm has been shown in Fig. 4(a).

All the grades of grafted sodium alginate have shown better flocculation efficacy than the polysaccharide (sodium alginate). This is due to their higher hydrodynamic volume (i.e. intrinsic viscosity) as evidenced in Table 1. The higher hydrodynamic volume of the macromolecule leads to higher flocculation efficacy (*Brostow, Pal and Singh model of flocculation*, Brostow, Pal, & Singh, 2007). There is a fine correlation evidenced for almost all grades of SAG-g-PMMA, as evident in Fig. 4. Thus, higher the percentage grafting, higher is the intrinsic viscosity. Higher the intrinsic viscosity, higher is the flocculation efficacy.

Evidently, among the various grades of SAG-g-PMMA, the optimized grade (SAG-g-PMMA 6) showed maximum flocculation efficacy due to its highest hydrodynamic volume (intrinsic viscosity).

The much higher flocculation efficacy of the grafted product than the original polysaccharide confirms the extension of Singh's easy approachability model (Singh, 1995; Singh et al., 2000) to grafted PMMA systems also (the model was primarily developed for grafted PAM systems).

For all the polymers studied, there is an optimal dosage at which the flocculation efficacy is maximum (i.e. the optical density of the supernatant collected is minimum), beyond which the flocculation decreases (i.e. optical density of the collected supernatant increases). This behavior of the flocculation curve finely confirms the *bridging mechanism* (Ruehrwein & Ward, 1952).

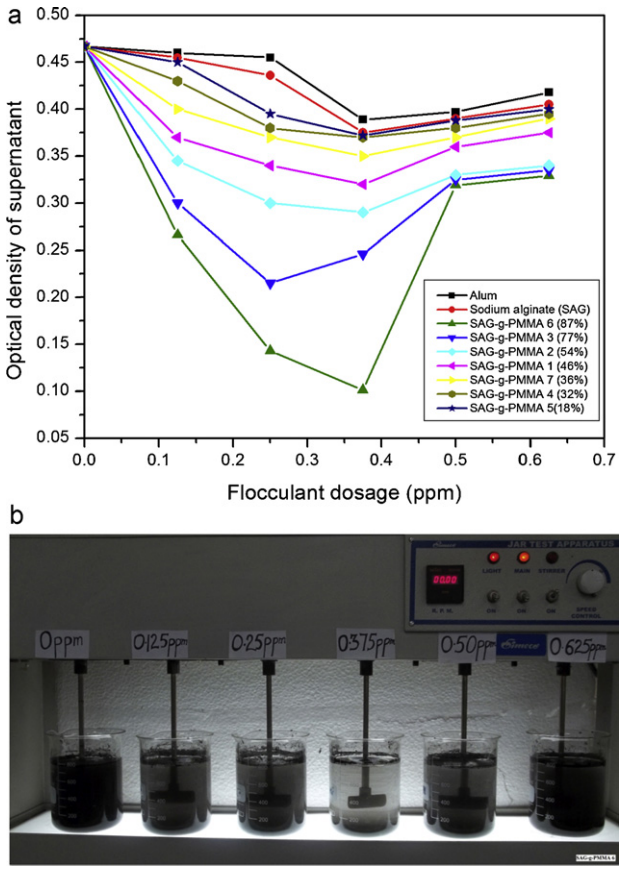


Fig. 4. (a) Flocculation profile in coal fine suspension and (b) jar test setup for flocculation profile of SAG-g-PMMA 6 in coal fine suspension.

The optimal dosage of SAG-g-PMMA 6 as flocculant, in 1% coal fine suspension is at 0.375 ppm. This extremely small dosage of SAG-g-PMMA indicates the miniscule amount of the chemical sufficient to effect flocculation. In more practical terms, the dosage translates to the fact that 1 gm of SAG-g-PMMA is sufficient for the treatment of 2667 l of coal washery effluent.

Further, also evident from Fig. 4(a) the dismayed performance of alum (coagulant) in treating the coal fine suspension at the dosage under study. Alum performed inferior than even sodium alginate.

A simple visual inspection (Fig. 4(b)) of the jar test procedure performed on coal fine suspension using SAG-g-PMMA 6 (optimized grade) as flocculant shows us its effectiveness in clarification of the suspension; specially at the optimized dosage of 0.375 ppm.

4. Conclusion

Polymethyl methacrylate grafted sodium alginate (SAG-g-PMMA) has been synthesized by *microwave assisted* technique. The synthesized grades of this graft copolymer were characterized through various physicochemical techniques. The increase in intrinsic viscosity due to grafting of PMMA chains opens the prospect of application of the grafted product as a superior viscosifier. Further, the flocculation efficacy of the graft copolymer was studied through standard jar test procedure in coal fine suspension and was compared to that of the starting material SAG and also with alum (coagulant) at an dosage ranging from 0 ppm to

0.675 ppm. SAG-g-PMMA grade with highest hydrodynamic volume (i.e. intrinsic viscosity) showed the maximum flocculation efficacy, as predicted by *'Brostow, Pal and Singh model of flocculation*'. The higher flocculation efficacy of the grafted product than the original polysaccharide also confirms the extension of '*Singh's easy approachability model*' to grafted PMMA systems. The high flocculation efficacy of SAG-g-PMMA in coal fine suspension makes it a superior flocculant than both the starting material (SAG) as well as alum (conventionally used as coagulant in municipal water treatment systems) for the treatment of coal washery effluents. The optimized dosage of flocculation for the best grade of SAG-g-PMMA has been found to be 0.375 ppm.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2012.08.023.

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