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Grafting of vinyl monomer onto gellan gum using microwave: synthesis and characterization of grafted copolymer

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In the presence of catalytic amount of ammonium persulfate as initiator, the grafting of polyacrylamide (PAAm) onto gellan gum (GG) was carried out using microwave irradiation. The grafting condition was optimized by varying the microwave power, exposure time, and concentrations of initiator, monomer, and GG. Fourier transform infrared spectroscopy, X-ray diffraction, and scanning electron microscopy analysis were employed to confirm that PAAm has been grafted onto the GG backbone. The intrinsic viscosity of pure and grafted samples has been measured by using Oswald viscometer. Swelling behavior of graft copolymer has been investigated and pH sensitivity of the graft copolymer was obtained. The flocculation characteristics of grafted and ungrafted polysaccharides have been evaluated in coal (coking and non-coking) suspensions. Graft copolymer shows better flocculation efficacy compared to the base polysaccharides.

Keywords: grafting; natural polymer; flocculation; swelling; optimization

1. Introduction

Gellan gum (GG) is an exopolysaccharide which is a gelling agent produced by *Pseudomonas elodea*.[1] The structure made up of repeating units of a tetrasaccharide composed of β-D-glucose, β-D-glucuronic acid, and α-L-rhamnose residues in the molar ratio of 2:1:1.[2,3] Natural GG has two acyl-substitute positions (O-acetate and L-glycerate), which individually join to the C-6 and C-3 positions of the same glucose molecule. The average molecular weight of GG is about 500 kDa.[4] It is a food additive that functions as a stabilizer, thickening agent, and versatile gelling agent in a wide variety of foods. GG has been investigated as a candidate material for biomedical engineering because of its biocompatibility and low cytotoxicity.[5] It has also been tested as a drug delivery carrier, cell carrier, guided bone-regeneration material, and wound dressing. However, biodegradability of GG reduces shelf life and needs to be controlled.

Extensive interests have shown on chemical modification of natural polymers for imparting attractive properties onto them. In recent years, chemical modification of natural polymers through grafting has received widespread attention and has paramount contribution towards their improved industrial applications.[6,7]

It has been reported that the grafting of polyacrylamide (PAAm) onto guar gum gives stability towards biodegradation and drag-reducing properties can also be

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*Corresponding author. Emails: tapan_ju01@rediffmail.com, tapan.giri@nshm.com enhanced.[8,9] Natural polysaccharides like xanthan gum, acacia gum, sodium alginate, starch, and carrageenan have been grafted onto PAAm in the past few years.[10–14] These grafted polymers improve flocculation efficiency, increase the solution viscosity, improve the drag-reduction effectiveness, impart resistant to biodegradation, and prepare controlled drug delivery system.[15–18]

The best method of graft copolymer synthesis is by use of microwave radiation to produce the free radical sites on the backbone polymer. Microwave heating can result fast transfer of the energy into bulk of the reaction mixture, and the depth of the materials is of the same order of magnitude of the wavelength and thereafter can interact with substances of considerable thickness. Microwave-based grafting is of two types. The most commonly used method employs microwave in the presence of a free radical initiator (microwave-assisted grafting).[19] The lesser known method involves microwave radiation in the absence of any free radical initiator (microwave-initiated method).[20] Microwave-assisted method exhibits the most excellent potential for synthesizing graft copolymers, because the free radicals are generated using microwave photons as well as free radical initiators, leading to a much higher percentage of grafting efficiency as compared to the conventional method of synthesis. We have synthesized polyacrylamide-grafted GG by microwave-assisted method in the presence of ammonium persulfate (APS) as free radical initiator.

2. Materials and methods

2.1. Materials

GG was procured from Applied Biosciences (Mumbai, India). Acrylamide (AAm) and APS were purchased from Loba Chemie, Mumbai, India. Methanol was purchased from Merck, Mumbai, India. All the chemicals used were of analytical grade and used as received.

2.2. Synthesis of AAm-grafted GG

Requisite quantity of GG was dispersed in 25 mL of water and allowed to swell overnight. AAm was mixed with 5 mL of water and added to the above mixture and stirred for about 1 h. Specified amount of APS was dissolved in 5 mL of water and added to the above dispersion. The dispersion was irradiated by microwave in domestic microwave oven (20STP21, MIRC Electronics Ltd., Mumbai, India) for different times and different powers to prepare series of graft copolymer. The reaction mixture was cooled and then excess of methanol was added to it and left overnight. The homopolymer was removed from the graft copolymer by solvent extraction using a formamide–acetic acid mixture (1:1 by volume).[21] The product was washed with aqueous methanol and filtered. The grafted gum thus prepared was vacuum dried at 45 °C to constant weight. The percentage grafting (%G) and percentage grafting efficiency (%GE) were calculated using the following equations:

$$\%G = \frac{(w_1 - w_0)}{w_0} \times 100 \tag{1}$$

$$\%\mathrm{GE} = \frac{(w_1 - w_0)}{w_2} \times 100 \tag{2}$$

where w_0 = weight of polysaccharide taken, w_1 = weight of graft copolymer, and w_2 = weight of AAm taken.

2.3. Fourier transform infrared spectroscopy

The samples were analyzed using a Fourier transform infrared spectrophotometer (Prestige-21, Shimatzu, Japan) in the range of 4000 to 400 cm^{-1}. Prior to the measurement, the samples were dried under vacuum until reaching a constant weight.

2.4. X-ray diffraction study

X-ray diffractogram of samples were recorded employing X-ray diffractometer (Ultima-III, Rigaku, Japan) in the differential angle range of 0 to 60° (2θ).

2.5. Scanning electron microscopy

Scanning electron micrographs of samples were taken using a scanning electron microscope (JSM6360, JEOL, UK). The photomicrographs of samples were taken at an accelerating voltage at 17 kV at different magnifications.

2.6. Flocculation properties

Flocculation experiments were carried out using a dissolution test apparatus (TDT-08L, Electro lab, Mumbai, India). About 500 mL of 1 wt% coal suspension was taken in dissolution rate test apparatus. Under a low stirring condition, required quantity of polymer solution was added to make predetermined dose with respect of suspension volume. After the addition of polymer solution, the suspension was stirred at a constant speed for 15 min. The flocks were allowed to settle down for half an hour. Afterwards, supernatant liquid was collected and turbidity was measured in a calibrated nephelo-turbidity meter (Model-341, EI lab, Himachal Pradesh, India) to express the turbidity in nephelometric unit (NTU).

2.7. Intrinsic viscosity measurement

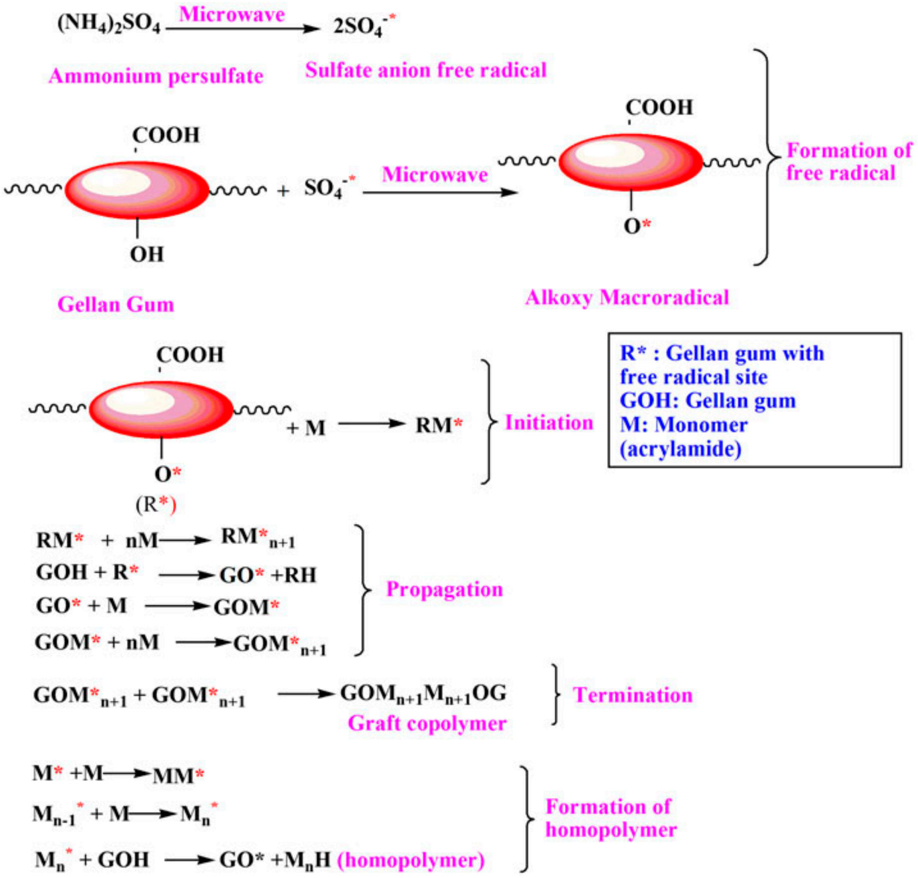
Intrinsic viscosities of polymer solutions were carried out with Oswald viscometer. The time of flow for solutions was measured at five different concentrations (0.2, 0.4, 0.6, 0.8, and 1% w/v). From the time of flow of polymer solutions (t) and that of the solvent (t_o), relative viscosity ($\eta_{\text{rel}} = t/t_o$) was obtained. Specific viscosity was calculated from the relation $\eta_{\text{sp}} = \eta_{\text{rel}} - 1$. Then, the reduced viscosity (η_{sp}/C) and the inherent viscosity ($\ln\eta_{\text{rel}}/C$) 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 vs. C and $\ln\eta_{\text{rel}}/C$ vs. C, and then take common intercept at $C = 0$ of the best-fitted straight lines through the two sets of points.[22]

2.8. Swelling studies

Swelling behavior of the graft copolymer was performed by tea-bag method. About 200 mg of sample was added to a small bag made of nylon (200 mesh). Then, the bag was completely immersed in the swelling medium (200 mL) at room temperature for 3 h to reach the swelling equilibrium. It was removed from the swelling medium and hung up for 15 min to remove the excess fluid and weighed. To investigate the swelling behaviors of the samples at various pHs, individual solutions were prepared by diluting NaOH (pH 12.0) and HCl (pH 1.0) solutions, respectively. To study the pH-responsiveness of the sample, buffer solution with pH 2 and 8 was used. The equilibrium swelling ratio was calculated as follows [23]: Equilibrium swelling ratio = (weight of swollen sample − weight of dry sample)/weight of dry sample.

3. Results and discussion

Grafted GG was synthesized by using microwave-assisted method. Sulfate ion radicals (SO_4^{-*}) were generated from the APS by the reduction of one electron under microwave. The SO_4^{-*} radicals abstract hydrogen atom from GG molecule producing GG macroradical. The monomer molecules, which are in close vicinity of reaction sites, become acceptor of GG macroradicals, resulting in chain initiation and thereafter themselves become free radical donor to neighboring molecules leading to propagation. These grafted chains are ended by coupling to give graft copolymer. The scheme of free radical reaction is given in Scheme 1.



Scheme 1. Probable reaction mechanism for the synthesis of graft copolymer.

3.1. Characterization of graft copolymer

The infrared spectra of AAm, GG, and AAm-grafted GG are shown in Figure 1. The spectra (Figure 1(a)) of AAm presented absorption bands at 3352.28 cm^{-1} due to asymmetric NH stretching and at 3180.61 cm^{-1} due to symmetric NH stretching of NH_2 group. The amide-I band (CO stretching) appears at 1674.21 cm^{-1} and amide-II (NH bending) appears at 1524.6 cm^{-1}. The band at 1429.25 cm^{-1} can be attributed to CN stretching, while the CH stretching appears at 2812.21 cm^{-1}. In the infrared spectra of GG (Figure 1(b)), a broad band, which appeared at 3416.79 cm^{-1}, could be attributed to the O–H stretching of hydroxyl groups of glucopyranose ring. Bands appeared at 1604.77 and 1413.82 cm^{-1} due to asymmetric and symmetric stretching of carboxylate (COO^-) group. The peak at 894.97 cm^{-1} was due to C–O–C skeletal of glycosidic linkages. The stretching vibration of $–CH_2$ groups and hydroxyl C–O–H was observed at 2922.15 and 1033.84 cm^{-1}, respectively. AAm-grafted GG (Figure 1(c)) shows characteristic peak at 3196.04 cm^{-1} due to NH_2 group, in addition of AAm which was grafted onto GG. Peak at 1041.56 cm^{-1} is also seen due to $CH–O–CH_2$ group which occurs due to grafting reaction between OH group of GG and π bond of AAm. A new peak appearing at 1450.46 cm^{-1} corresponding to C-N bending vibration also supports the grafting reaction.

The X-ray difftractogram of AAm, GG, and grafted GG are shown in Figure 2(A). The diffractogram of AAm (Figure 2(A)(a)) showed the crystalline nature of AAm. There is no considerable peak of crystallinity in the spectrum of GG (Figure 2(A)(b)). Graft copolymer shows single amorphous structure as demonstrated by broad halo (Figure 2(A)(c)). It is thus concluded that grafting leads to disruption in the original crystalline structure of AAm.

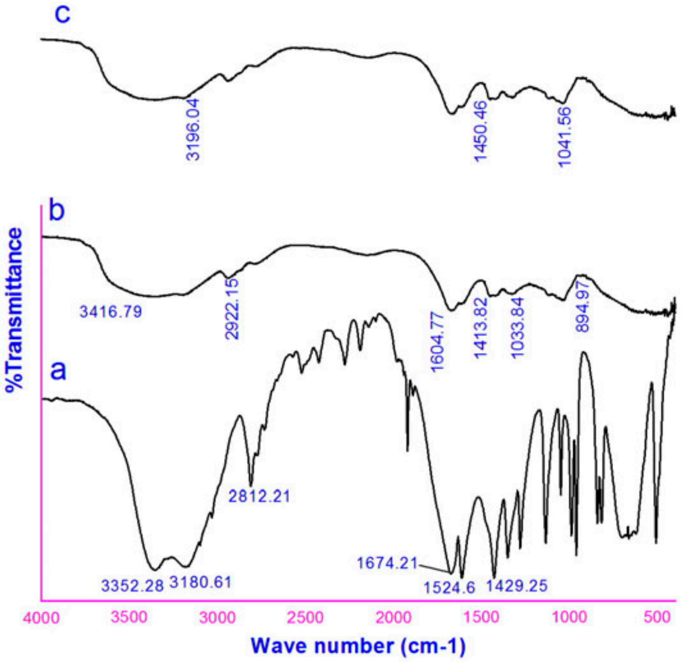


Figure 1. Infrared spectra of (a) AAm, (b) GG, and (c) AAm-grafted GG.

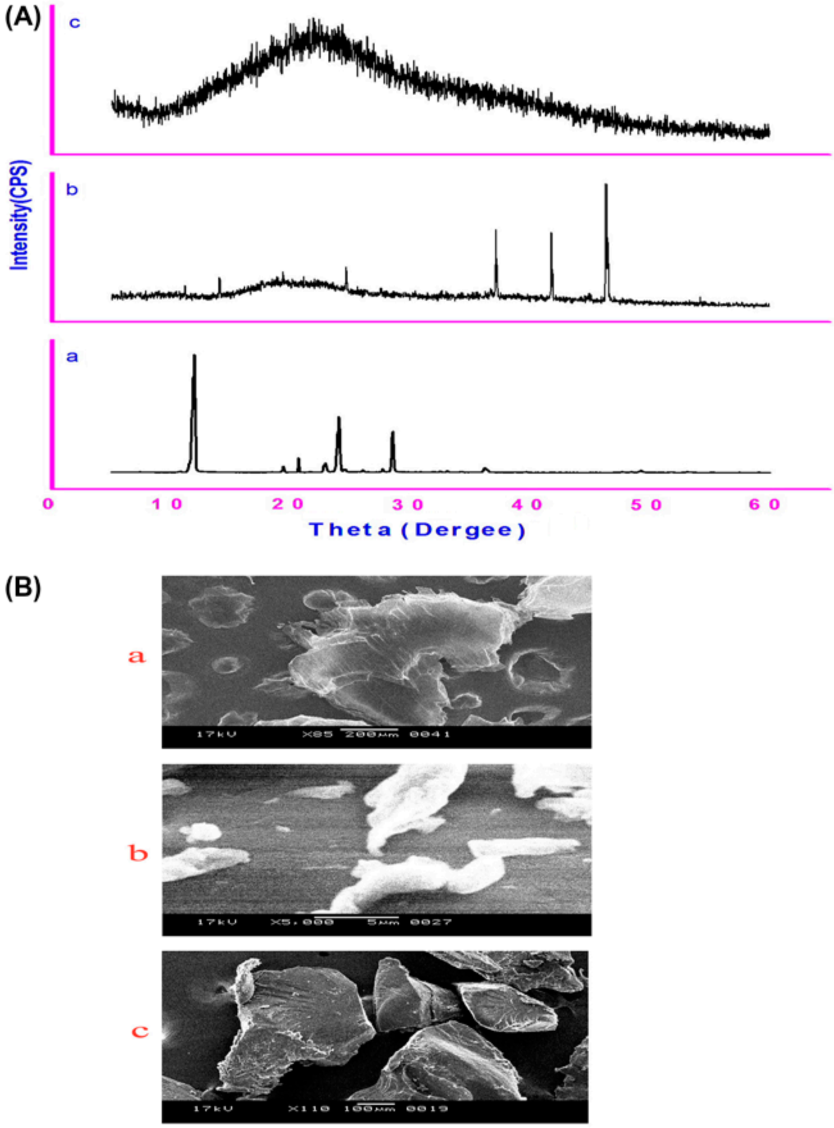


Figure 2. (A) X-ray diffractogram of (a) AAm, (b) GG, and (c) AAm-grafted GG. (B) Scanning electron micrograph of (a) AAm, (b) GG, and (c) AAm-grafted GG.

Figure 2(B) shows the scanning electron micrographs of AAm, GG, and AAm-grafted GG. The AAm particles (Figure 2(B)(a)) are polyhedral in shape, while the GG (Figure 2(B)(b)) particles are fibrous in nature. The scanning electron micrograph images of grafted copolymer (Figure 2(B)(c)) shows that the grafting of AAm onto GG brings about the change in the shape and size of the GG particles. It is noticed that grafted copolymer particles are of larger dimensions than the native gum particles. The grafting introduces changes on the surface and size of the GG particles.

3.2. Optimization of the grafting conditions

The optimum reaction condition was obtained by varying the concentration of APS, GG, and AAm along with reaction time and microwave power, and their effect on grafting parameters has been studied.

3.2.1. Effect of APS concentration

The effect of the APS concentration on grafting reaction was studied by varying the concentration of APS from 0.5×10^{-3} to 50×10^{-3} mol/L (Figure 3(a)). There was an increase in grafting parameters as the concentration was increased to 30×10^{-3} mol/L, but

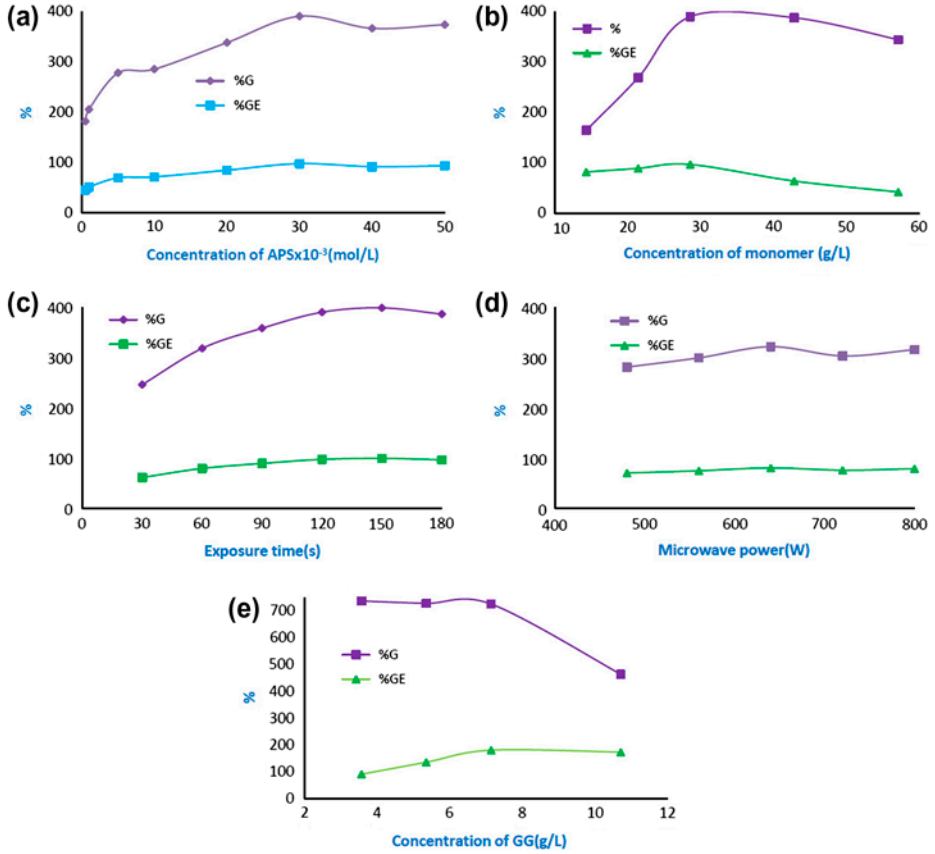


Figure 3. (a) Effect of initiator (APS) concentration keeping other variables constant at [GG] = 7.143 g/L; [AAm] = 28.57 g/L; reaction volume = 35 mL; reaction time = 120 s, microwave power = 640 W. (b) Effect of AAm concentration keeping other variables constant at [GG] = 7.143 g/L; [APS] = 30×10^{-3} mol/L; reaction volume = 35 mL; reaction time = 120 s, microwave power = 640 W. (c) Effect of exposure time keeping other variables constant at [GG] = 7.143 g/L; [APS] = 30×10^{-3} mol/L; [AAm] = 28.57 g/L; reaction volume = 35 mL, microwave power = 640 W. (d) Effect of microwave power keeping other variables constant at [GG] = 7.143 g/L; [APS] = 30×10^{-3} mol/L; [AAm] = 28.57 g/L; reaction volume = 35 mL, time = 150 s. (e) Effect of GG concentration keeping other variables constant at [APS] = 30×10^{-3} mol/L; [AAm] = 28.57 g/L; reaction volume = 35 mL, time = 150 s, microwave power = 640 W.

thereafter, these parameters decreased. Increase in grafting parameters with increasing APS concentration up to a definite value may be ascribed to an increase in the concentration of free radicals produced by APS resulting in the production of GG radicals at a faster rate. A comparatively high concentration of the initiator may cause a reduction of grafting due to an increase in the number of GG radicals ended prior to AAm addition. Furthermore, homopolymerization formation at higher initiator concentrations which compete with the grafting reaction for available monomer could lead to a decrease in the percentage of grafting. Similar observation was made by other authors [24].

3.2.2. *Effect of AAm concentration*

The effect of AAm on graft copolymerization has been studied by varying the concentration of AAm from 14.28 to 57.14 g/L (Figure 3(b)). It has been found that grafting parameters were increased with increasing the concentration of AAm from 14.28 to 28.57 g/L, but beyond 28.57 g/L, these grafting parameters were decreased. This activity could be explained by the fact that an increase of monomer concentration leads to the buildup of monomer in close proximity to the backbone and gives rise to graft copolymerization. However, at higher monomer concentration, the primary radicals attacked the monomer instead of reacting with the backbone polymer, thereby initiating homopolymerization reaction, and thus the low grafting parameters were observed beyond optimum monomer concentration. Similar observation was made by other authors [25].

3.2.3. *Effect of exposure time*

The effect of the time period on the grafting parameters was studied through the variation of the time period of the reaction from 30 to 180 s (Figure 3(c)). It has been observed that grafting parameters were increased with increasing the time period from 30 to 150 s, but beyond 150 s, these grafting parameters were decreased. On further increasing the time period, grafting parameters show decreasing trend. On increasing the time period, proliferation of grafting chains takes place due to availability of more macroradicals, which accounts for higher grafting. After 150 s, decrease in grafting parameters may be ascribed to the development of more homopolymer. Similar observation was made by other authors [26].

3.2.4. *Effect of microwave power*

Grafting was carried out at different microwave powers ranging from 480 to 800 W (Figure 3(d)). Grafting was found to increase with increase in microwave power up to 640 W and further increase in microwave power resulted in decreased grafting parameters. This activity could be explained on the basis that as the microwave power was increased, more macroradicals were generated, which resulted increase in grafting parameters. After 640 W, decrease in grafting parameters may be ascribed to the formation of more homopolymer at high microwave power or to some decomposition of the graft copolymer. Similar observation was made by other authors [27].

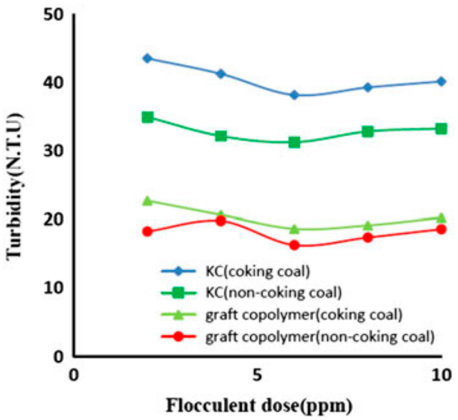


Figure 4. Flocculation characteristics of graft copolymer in coal suspension.

3.2.5. Effect of GG concentration

Figure 3(e) shows the effect of the concentration of GG on the grafting parameters. Percent grafting decreases gradually with the increased GG concentration. However, percent grafting efficiency increases at first and afterward declines. An increase in backbone concentration can make more monomers and initiators simply approachable to the surface of GG produce more grafted side chains which cause increase in percent grafting efficiency. The decreasing trend of grafting parameters may be due to the high viscosity of the reaction system that makes the diffusion of both monomer and initiator to GG difficult. Similar observation was made by other authors [26].

3.3. Flocculation properties

Plots of supernatant turbidity vs. polymer dosage for coking and non-coking coals are given in Figure 4. It has been found that grafted copolymer gives superior performance by showing lower turbidity than GG itself. In case of the graft copolymers, the dangling grafted chains have better approachability [28] towards the colloidal particles than the linear polymers of similar nature in a same colloidal suspension. Another reason for the better flocculating power of the graft copolymers over the linear polymers is polymer bridging. In order for successful bridging to occur, there must be adequate polymeric chains, which extend far enough from the particle surface to attach to other particles. In the case of linear polymers, the polymer segments attached to the surface in trains project into the solution as tails or form part of loops, which links trains together.[29] By this way, they can form bridges between the colloidal particles to form flocks. But for the graft copolymers, the dangling grafted chains can easily bind the colloidal particles through bridging to form flocks. This type of intense bridging is not possible in the case of linear polymers. The differences in turbidity value in coking and non-coking coal in coal suspension is due to the difference in negative charge density, which is higher in non-coking coal in aqueous solution.[30]

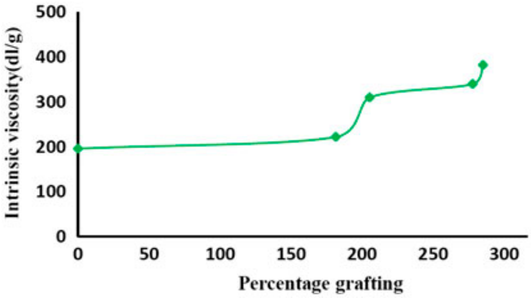


Figure 5. Intrinsic viscosity vs. percentage grafting plot for graft copolymer.

Table 1. Intrinsic viscosity of various grades of graft copolymer.

Grades	% grafting	Intrinsic viscosity (dL/g)
GG	0	196
GG-g-PAAm1	181.56	222
GG-g-PAAm2	205.39	310
GG-g-PAAm3	277.91	340
GG-g-PAAm4	285.22	382

3.4. *Intrinsic viscosity measurement*

The intrinsic viscosity was evaluated for GG and the different grades of graft copolymer, as shown in Table 1. Intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution that is a function of the polymer molecular weight, its structure, the nature of the solvent, and the temperature of the medium.[31] It is evident from Table 1 that the intrinsic viscosities of all the grades of graft copolymer are greater than that of GG. This is due to the increase in hydrodynamic volume resulting from grafting of the PAAm chains on the GG backbone.[32] 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 attributes the increase in intrinsic viscosity to the increase in molecular weight (M) due to the grafted PAAm chains. The relationship between percentage grafting and intrinsic viscosity of various grades of graft copolymer has been plotted in Figure 5. The intrinsic viscosity of graft copolymer increases with increase in percentage of grafting.

3.5. *Swelling study*

The equilibrium swelling of the samples were studied at various pHs ranged from 1 to 12. As depicted in Figure 6(a), at the low pH values, the equilibrium swelling capacity of samples is low. As increasing the pH value of external solution, the equilibrium swelling capacity increased up to pH 8. Then, the swelling capacity decreased when the pH value reaches beyond 8. Under acidic pH values, most of the carboxylate anions are protonated, so the main anion–anion repulsive forces are eliminated and consequently swelling values are decreased. At higher pH values, some of the carboxylate

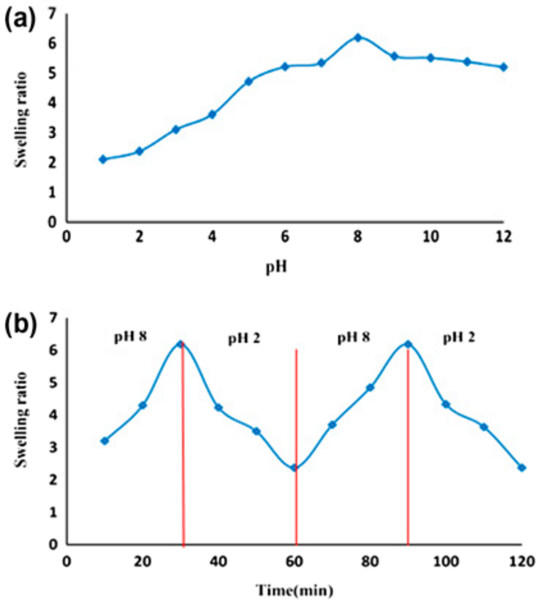


Figure 6. (a) Swelling behavior of graft copolymer at different pH and (b) pulsatile swelling.

groups are ionized and the electrostatic repulsion between COO– groups causes an enhancement of the swelling capacity. Again, a charge screening effects of the counterions (cations) limits the swelling at higher basic pH values ($pH > 8$).[33]

The pH-dependent swelling reversibility of the graft copolymer was investigated in buffer solution with pHs 2 and 8 (Figure 6(b)). In pH 8 buffer solution, the graft copolymer was quickly swelled due to the ionization of COOH groups and anion–anion repulsive electrostatic forces among COO– groups. When the swollen graft copolymer was immersed in pH 2 solution, it rapidly deswells and the gel network collapsed because of the protonation of carboxylate groups in acidic media. Such on–off (swelling–deswelling) switchable swelling activities of the polymer make them as a prospective candidate for controlled drug delivery system.

4. Conclusion

Graft copolymers of GG and PAAm were effectively synthesized using microwave-assisted method. The optimum grafting was observed when the reaction mixture containing 30×10^{-3} mol/L APS; 28.57 g/L AAm; 7.14 g/L GG; was exposed to 640 W microwave power for 150 s. The synthesized grades of this graft copolymer were characterized through various physico-chemical techniques. The increase in intrinsic viscosity due to grafting of PAAm chains opens the prospect of application of the grafted product as a superior viscosifier. The synthesized graft copolymer shows improved results for flocculation in comparison to parent polysaccharide. It is concluded that synthesized graft copolymer could be utilized very well industrially.

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