

Microwave Promoted Grafting of Acrylonitrile onto *Cassia siamea* Seed Gum

Vandana Singh, Devendra N. Tripathi

Department of Chemistry, University of Allahabad, Allahabad 211002, India

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ABSTRACT: *Cassia siamea* seed polysaccharide was grafted with acrylonitrile under microwave (MW) irradiation without adding any radical initiator or catalyst. Free radicals are generated here due to the dielectric heating caused by the localized rotation of the hydroxyl groups at the polysaccharide backbone and initiate grafting. To obtain the optimal conditions for the microwave promoted grafting, effect of reaction variables such as monomer/seed gum concentration; MW power and exposure time on the graft copolymerization was studied and the maximum %grafting (%G) and %efficiency (%E) observed were 150% and 43.54%, respectively. The representative graft copolymer was characterized by Fourier transform-infrared, Thermogravimetric

analysis and X-ray diffraction measurement, taking *C. siamea* gum as reference. At the same monomer concentration, $K_2S_2O_8$ /ascorbic acid initiated grafting onto the seed gum could result into 80% grafting with 23.22% efficiency. Various properties of the MW synthesized grafted gum like water/saline retention, water retention after saponification and viscosity of the gum solutions were studied. The results have been compared with the conventionally synthesized grafted gum and the parent gum. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 2384–2390, 2006

Key words: polysaccharide; graft copolymer; microwave irradiation; viscosity; gel formation; water/saline retention

INTRODUCTION

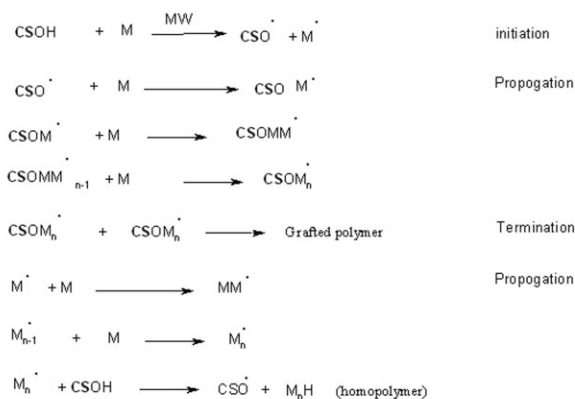
Cassia siamea (CS) is a medium sized tree of great medicinal importance,¹ it has long leaves and bright yellow flowers and is distributed over western peninsula¹ in India. Its seed endosperm has been reported to contain a substantial amount of a complex polysaccharide² containing D-galactose, D-mannose, and D-xylose as component sugars in 3 : 6 : 2M ratio respectively. Vinyl and vinylidene grafting onto the seed gums is reported^{3–8} to incorporate favorable properties in them while retaining their desirable properties such as viscosity, water/saline retention, and film/gel formation. Grafted Guar gum (GG) is used in the preparation of flocculants^{9,10} for the industrial effluents treatment and as biodegradable drag reducing agents.¹¹ Crosslinked Guar-graft-polyacrylamide based anionic microgels for a pH sensitive drug delivery has been recently reported.¹² Lokhande et al.¹³ prepared water supersorbent guar-modified polymers by grafting of acrylonitrile onto GG through γ -radiation.

Microwave irradiation¹⁴ has been exploited in various fields of chemistry including polymers. Grafting

of butylacrylate,¹⁵ acrylic acid,¹⁶ and acrylonitrile¹⁷ onto the starch, grafting of acrylamide onto low density polyethylene films,¹⁸ and grafting of butyl methacrylate onto the wool fibers¹⁹ has been studied recently under microwave irradiation. Methylmethacrylate has been polymerized²⁰ under microwave with very low concentration of the initiators. Recently our group has reported the grafting of poly(acrylonitrile)²¹ onto the polysaccharides like chitosan and guar gum²² under microwaves without using any catalyst and redox initiator. Under microwaves, grafting of poly(acrylamide)²³ onto the guar gum was also done successfully in very short time. Using microwave irradiation^{21,23} higher or comparable %G and %E can be obtained as compared to conventional grafting procedures while saving the time and chemicals both. Since acrylonitrile grafting^{4,22,24,25} is reported²⁶ to impart interesting properties to the seed gums, in the present study acrylonitrile was selected for the grafting onto CS gum under microwave irradiation. Many redox systems have been reported^{27–30} in literature for acrylonitrile grafting onto the seed gums, $K_2S_2O_8$ /ascorbic acid system is selected for the comparison with microwave method as this system gives better %G and %E as compared to other systems^{22,24,25} and also does not require inert atmosphere.³¹ To understand the advantage of microwave promoted grafting over the conventional grafting, %G and %E for both the methods were compared. Properties of the microwave synthesized grafted gum and the conventionally synthesized

Correspondence to: V. Singh (singhvandanasingh@rediffmail.com).

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Where CS stands for Cassia siamea seed gum
 M stands for acrylonitrile
 MW for microwave irradiation

Scheme 1 Mechanism of grafting under microwave irradiation.

grafted gum were studied and compared with the parent CS gum for exploring the possibility of the commercial utilization of the CS/grafted CS gum.

EXPERIMENTAL

A Kenstar (Model No. OM 20 ESP; 800W) domestic microwave oven was used for all the experiments. The average bulk temperature at the end of the reaction was measured by inserting thermometer in the reaction mixture and was less than 100°C. All the reactions were performed in aqueous medium. CS seed gum was supplied by Himani seed stores, Deheradun, and identified by systematic botanist at Botanical Survey of India, Allahabad. Acrylonitrile (Lancaster, synthesis grade) was distilled in a stream of nitrogen before use ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification. Infra red (IR) spectra were recorded on a Perkin-Elmer IR spectrophotometer using KBr pellets. X-ray diffraction (XRD) was carried out on Isodebexlex 2002 X ray powder diffractometer and TGA was carried out on Perkin-Elmer Pyris 6TGA in N₂ atmosphere. Sample with maximum grafting yield was selected for characterization by spectral studies.

The percentage and efficiency of grafting were calculated according to Kojima et al.³²

$$\% \text{Grafting} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

$$\% \text{Efficiency} = \frac{W_1 - W_0}{W_2} \times 100 \quad (2)$$

where W_1 , W_0 , and W_2 denote, respectively, the weight of the grafted seed gum, weight of original seed gum, and weight of the monomer used.

Graft copolymerization

Grafting under microwave irradiation

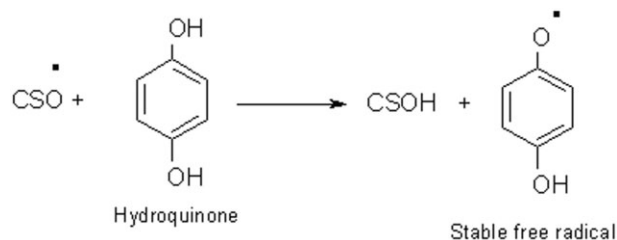
To a solution of CS seed gum (0.1 g in 25 mL water), a known amount of acrylonitrile was added and the reaction mixture was irradiated in a domestic microwave oven in a 150 mL flask. Reaction was repeated with different monomer concentration in the range of 8.8×10^{-2} – 28×10^{-2} mol/L, MW power and exposure time. The reaction product was precipitated *N,N*-dimethylformamide (DMF). It was again subjected to Soxhlet refluxing for 8–12 h using DMF to solubilize and remove the homopolymer. %Grafting and %efficiency were calculated. Maximum %G achieved was 150% with efficiency of 43.54% at 100% MW power using 26×10^{-2} mol/L acrylonitrile concentration at 95°C in 2.0 min. The reaction was repeated with 20 mg hydroquinone (HQ) (radical scavenger) under optimal grafting conditions.

Grafting⁴ using K₂S₂O₈/ascorbic acid redox pair under thermostatic water bath

To a solution of CS gum (0.1 g in 25 mL water) taken in a 150 mL reaction flask, acrylonitrile (26×10^{-2} mol/L) and ascorbic acid (2.3×10^{-2} mol/L) were added and thermostated on water bath at (35±2)°C. After 30 min K₂S₂O₈ (1×10^{-3} mol/L) was added and this time of addition of persulphate was taken as zero time. Graft copolymerization was allowed for 1 h. Then the reaction product was precipitated DMF as described above and %Grafting and %efficiency were calculated (%G 82% and %E 23.22%).

Determination of water and saline retention⁴

An accurately weighed amount of the dried polymer was placed in a previously dried and weighed sintered glass crucible (G-4), which was then filled with 50 mL of water and after 30 min suction from a vacuum pump was applied. The glass crucible was then weighed to determine the amount of water retention per gram of the dried material and this was taken as water retention capacity. Similarly saline retention capacity was determined by using 1% aqueous sodium chloride solution.



Scheme 2 Quenching by hydroquinone.

Hydrolysis in aqueous alkali

Grafted CS gum sample with maximum %G was hydrolyzed³² in aqueous alkali. Two grams of grafted sample (on dry basis) was dispersed in 1% NaOH at 100°C for 1.5 h. The hydrolyzate was then precipitated in 600 mL methanol, washed with methanol and ethanol, dried and weighed.

Water retention of the alkali hydrolyzed samples

Alkali-hydrolyzed sample (0.5 g) (on dry basis) was swollen³³ in 100 mL distilled water for 30 min. The suspension was poured into sintered glass filter (porosity 1) at 700 mmHg pressure. The volume of the filtrate was measured and water retention was calculated as gram of water per gram of the dry material. The measurement was repeated after drying the hydrolyzed sample in an oven at 60°C.

Viscosity measurements³⁴

For preparing gum solutions, weighed quantity of the gum/grafted gum were dissolved in the minimum quantity of water and then gum solutions were made up to a desired concentration and agitated vigorously for about 15 min till the solutions became viscous and homogeneous. The measurements were made using small sample adapter (spindle no S-18) of Brookfield LVDVE viscometer at 30°C.

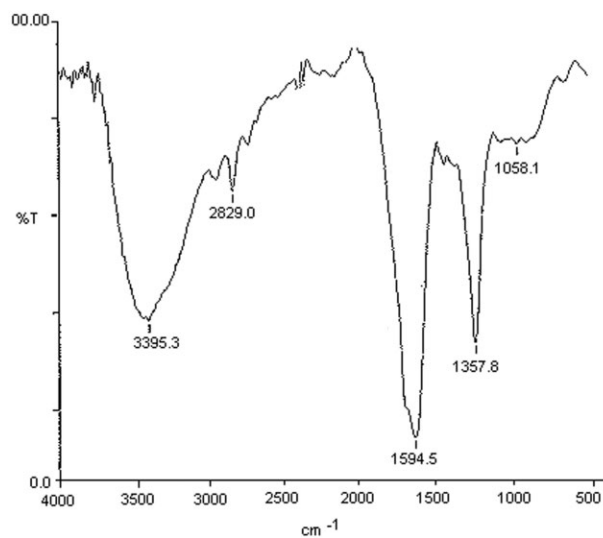
Gel formation

Gel³⁴ was prepared by adding known amount of borax to 8 mL solution of the gum/grafted gum of the known concentration, followed by the shaking. Time required for the gel formation with different amount of the borax and the viscosities of the resulting gels were measured. For the same concentration of the gum solutions higher gelling time was observed for the grafted gums as compared to parent CS gum under the studied concentration range of the borax. The gel with the seed gum was found to be reversible in nature and dissolved on heating or changing the pH to 3 or 9.5 by adding 1N HCl or 0.01N NH₄OH solutions to the gel. Gel from the grafted gum also behaved similarly except that when 0.01N NH₄OH was added the gel become stringy instead of dissolving.

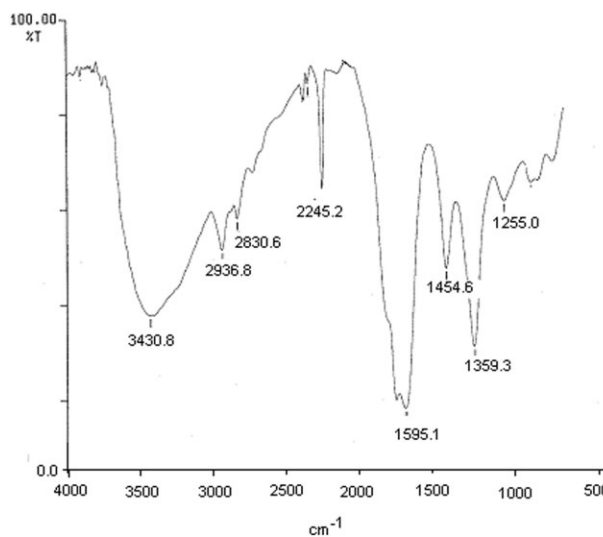
RESULTS AND DISCUSSION

Characterization of the grafted *Cassia simea* gum

Graft copolymer based on CS has been synthesized by grafting acrylonitrile onto the polysaccharide molecule in aqueous medium using microwave irradiation. IR spectrum of pure CS gum has broad strong bands at 3395 and 2829 cm⁻¹ due to O—H and C—H stretch-



(a)



(b)

Figure 1 (A) IR spectra of pure *Cassia siamea* gum. (B) IR of the microwave synthesized CS-g-PAN.

ing respectively, while IR Spectra of MW grafted CS gum has additional strong absorption peaks at 2245 cm⁻¹ for —CN stretching and CH₂ deformation vibration at 1454 cm⁻¹ (Fig. 1). Physical blend of CS gum and poly(acrylonitrile) after selective removal of poly(acrylonitrile) with DMF showed no absorption in —CN stretching and —CH₂ bending region. This substantiates the formation of the graft copolymer and not the mere blending of the two. The grafting was also supported by XRD (Fig. 2) and TGA (Fig. 3). It is obvious that the XRD spectra of the grafted seed gum show crystalline areas in the region of 2θ 28–32° (because of poly(acrylonitrile) grafts), while the CS seed gum show amorphous nature. TGA of CS (A) seed gum shows a weight loss in two stages. The first stage

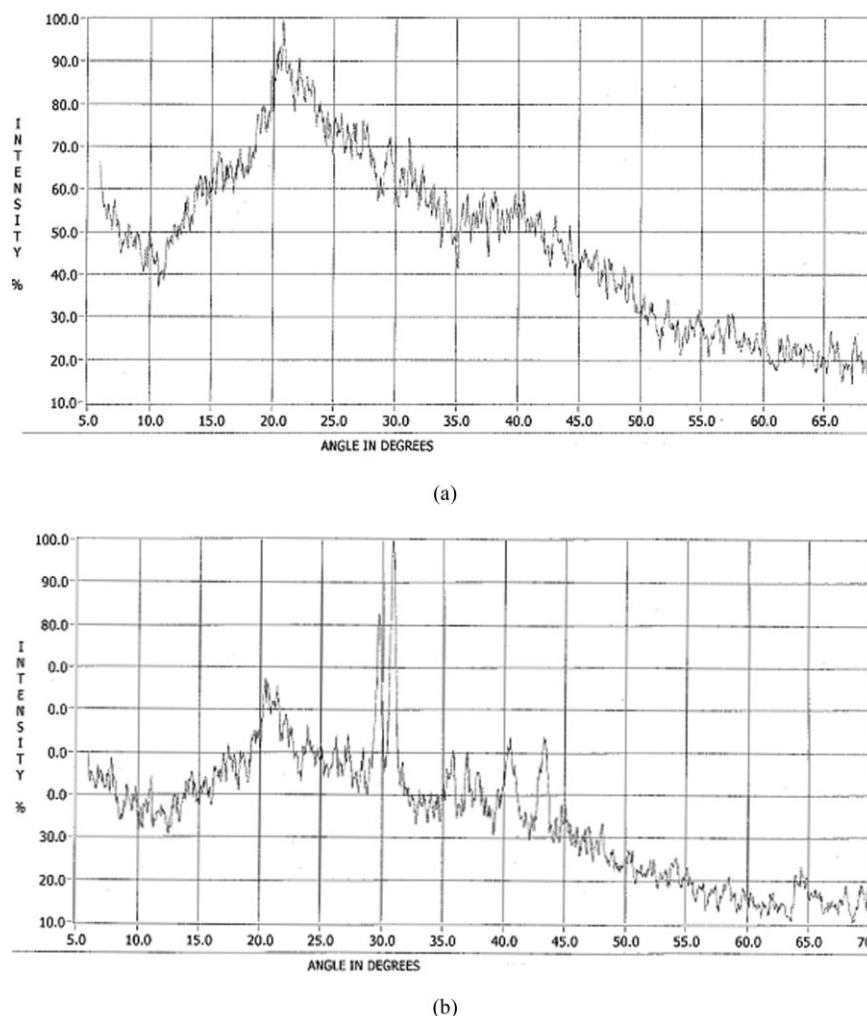


Figure 2 (A) XRD spectra of pure *Cassia siamea* seed gum. (B) XRD spectra of microwave synthesized CS-g-PAN.

ranges between 35 and 160°C and shows about 13% loss in weight and may be due loss of adsorbed and bound water. In the second stage the decomposition onsets at 275°C and continues up to 320°C showing 47% weight loss due to the degradation of the seed gum. TGA of the grafted product (B) shows first weight loss of about 6% between 35 and 100°C due to adsorbed and bound water loss indicating less water binding sites available at the grafted gum. The second stage of weight loss starts at 250°C and it continues up to 315°C indicating 36% weight loss. Up to 500°C, a total weight loss of ~78% was observed in *C. simeae* seed gum in comparison with 62% weight loss in the grafted CS gum showing the grafted gum to be more thermally stable.

Formation of free radicals under microwave irradiation

Since the grafting was not observed when radical scavenger (HQ) is added to the reaction mixture, a free

radical mechanism for the grafting is most probable. As no radical initiator is added, the grafting observed could be initiated by the generation of the free radicals under the influence of the microwaves that can be explained as follows.

CS molecule is a complex polysaccharide molecule and therefore its rotation is not expected to be observed under microwave region, however, the localized rotation¹⁷ of the pendent hydroxyl groups at the immobile polysaccharide molecule will be observed in the microwave region and resulting dielectric heating of the seed gum molecule may result in an enhancement of reaction rates specifically at these groups. The dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (acrylonitrile and water) as it is not possible to store the energy in a specific part of the molecule. In the CS gum there a large numbers of such —OH groups and therefore this energy amount is expected to be enormous and this may be responsible for OH bond-break-

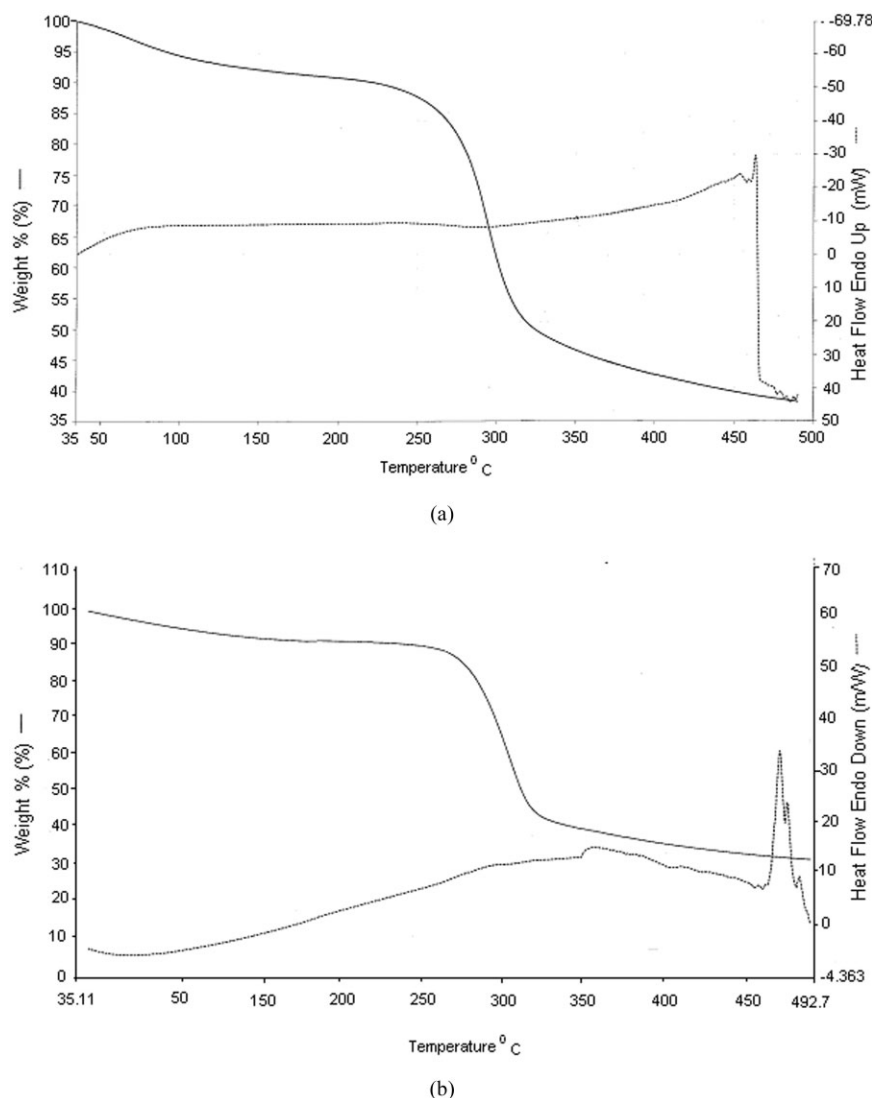


Figure 3 (A) TGA of pure *Cassia siamea* seed gum. (B) TGA of microwave synthesized CS-g-PAN.

ing. Further MW are also reported to have special effects¹⁸ of lowering of Gibbs energy of activation of the reactions and in view of the above two effects a plausible free radicals mechanism for the grafting under the microwave irradiation has been proposed (Scheme 1). —OH groups of the CS gum, being polar will absorb MW energy and will cleave generating monomer free radical that will initiate the graft copolymerization. Inhibition of grafting on addition of HQ further supports a free radical mechanism of grafting under microwaves.

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 results from delocalization of electron charge density throughout the aromatic structure, thus addition of HQ quench the grafting under microwaves which supports the free radical mechanism given (Scheme 2).

To find out the optimal conditions for the grafting under microwaves various reaction parameters were varied and the results were summarized.

Monomer effect

The grafting was found to increase with an increase in the initial concentration of monomer in the range of

TABLE I
%G and %E with Change in Monomer Concentration at 100% MW Power at 95°C After 2 min Exposure

Acrylonitrile (<i>M</i>)	%G	%E
8.8×10^{-2}	40	34.30
13×10^{-2}	80	46.44
17×10^{-2}	110	48.93
22×10^{-2}	130	45.90
26×10^{-2}	150	43.54

TABLE II
%G and %E With Change in MW Power and Exposure Time at Fixed Concentration of Acrylonitrile ($26 \times 10^{-2} M$), CS Gum (4 g/L), Total Reaction Volume (25 mL)

MW power	Temperature (°C)	Exposure time (s)	%G	%E
40%	52	30	30	8.7
	62	60	40	11.61
	81	90	45	13.06
	86	120	55	15.96
	55	30	40	11.61
60%	65	60	52	15.09
	84	90	68	19.73
	88	120	90	26.12
	62	30	55	15.96
	70	60	95	27.57
80%	90	90	105	30.47
	95	120	120	34.83
	80	30	65	18.86
	92	60	92	26.70
100%	95	90	115	33.38
	95	120	150	43.54

$8.8 \times 10^{-2} - 28 \times 10^{-2}$ mol/L, keeping other parameters fixed. (Table I) The increase in %G grafting with increase in acrylonitrile concentration may be due to the formation of more M_n radicals, which in turn may generate more grafting sites onto the seed gum by the abstraction of H atom. However on increasing concentration of the monomer beyond 17×10^{-2} mol/L, %E decreases probably because of homopolymer formation.

Effect of MW power and exposure time

%G and %E were found to increase with increase in MW power. At higher MW power more microwave energy is absorbed, resulting in more macroradicals and therefore the grafting yield and efficiency. Yield was found to increase with increase in exposure time at fixed MW power up to 2 min (Table II).

Effect of seed gum concentration

The increase in the seed gum concentration, while keeping other parameter fixed decreases the %G and

TABLE III
Change in %G and %E with Seed Gum Concentration at Fixed Concentration of the [AN] = $26 \times 10^{-2} M$ at 100% MW Power After 2 min Exposure

CS gum concentration (mg/mL)	%G	%E
100	150	43.54
150	146	42.38
200	116	33.67
250	106	30.76
300	94	27.28

TABLE IV
Water and Saline Retention of the *C. siamea* Seed Gum and Poly(acrylonitrile) Grafted *C. siamea*

Sample	Water retention (g/g)	Saline retention (g/g)	Water retention by saponified CS-g-PAN (g/g)
<i>Cassia siamea</i>	13.2	9.3	–
CS-g-PAN (Th)	8.7	6.4	29.18
CS-g-PAN (MW)	7.3	5.2	42.80

%E. Increased viscosity of the gum solutions at higher concentration may cause hindrance in normal grafting reaction (Table III).

Water and saline retention

The water/saline retention property is due to the interaction of the hydroxyl groups of the seed gums through hydrogen bonding (Table IV). The grafting of the vinyl monomers onto the seed gums occurs through the hydroxyl groups²⁹ of its backbone thereby decreasing the number of the hydroxyl groups and consequently water/saline retention capacity of the grafted gum. Decrease in the water/saline retention has been found proportional to the grafting percent. Since at similar monomer concentration %G was higher in MW method, decrease in water and saline retention in MW synthesized graft copolymer (sample synthesized under similar monomer concentration) is more prominent (Table IV). The polysaccharide under study has numerous adjacent hydroxyl groups in the cis position and therefore with borax are capable of giving three-dimensional gels while after grafting, some of the —OH sites in the seed gum are replaced with poly(acrylonitrile) grafts thereby decreasing the number of available cis —OH groups for the interaction with the gelling agent. Thus for gel formation of the grafted gums, higher concentration of the gelling

TABLE V
Gel Formation of 1% Solution (w/v) of *C. siamea* Gum and Grafted CS Gums

Gum	Amount of borax (mg)	time (s)	Viscosity (cP)
<i>C. siamea</i>	25	31	5340
	50	26	7030
	100	19	> 10,000
	150	19	> 10,000
	25	51	> 10,000
CS-g-PAN (Th)	50	43	> 10,000
	100	21	> 10,000
	150	13	> 10,000
CS-g-PAN (MW)	25	72	> 10,000
	50	58	> 10,000
	100	32	> 10,000
	150	24	> 10,000
	150	24	> 10,000

TABLE VI
Viscosity of the 1% Solutions (w/v) *C. siamea* and Grafted *C. siamea* Gum as Measured by Brookfield Viscometer

Sample	Viscosity (cP)
CS gum	49.8
CS-g-PAN (Th)	120.6
CS-g-PAN (MW)	162.5

agent is required (Table V). On PAN grafting viscosity of the gum solutions increased and MW grafted CS seed gum solutions had higher viscosity than the conventionally synthesized graft copolymer, this is explainable as MW synthesized graft copolymer has higher %G (Table VI).

CONCLUSIONS

CS-graft-poly(acrylonitrile) could be very efficiently synthesized without any radical initiator or catalyst in a very short reaction time of 2 min using 100% MW power at 26×10^{-2} mol/L acrylonitrile concentration. %G and %E achieved in the microwave method were higher than $K_2S_2O_8$ /ascorbic acid redox initiated grafting. PAN grafted CS seed gum samples have lower water/saline retention and gelling ability than parent seed gum, however, grafted gum solutions had higher viscosity and shelf life as compared to the parent gum solutions. Alkali hydrolyzed PAN grafted CS seed gum absorbs significant amount of water.

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