Alumina-Supported Microwave Synthesis of Cassia marginata Seed Gum-*graft*-Polyacrylamide

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ABSTRACT: In this article, we report the alumina-supported, microwave (MW)-induced synthesis of *Cassia marginata* seed gum-*graft*-polyacrylamide (MWS-GP). No initiator or catalyst was required in the synthesis, and the conditions for the grafting were optimized by variation of the acrylamide concentration, MW power, and exposure time. At an identical monomer concentration, a higher level of grafting was observed in the solid-supported method than under aqueous conditions (the MW-assisted or redox-initiated thermal method). The used alumina support was easily separated from MWS-GP and reused for another three cycles without any significant loss in its efficiency as a solid support. MWS-GP synthesized under optimum conditions was characterized with Fourier transform infrared spectroscopy, ^{13}C-NMR, thermogravimetric analysis, and X-ray diffraction, with *C. marginata* gum as a reference. The properties of MWS-GP and its saponified derivative were studied to explore the applicability areas of the copolymer in hydrogel formation. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 3630–3638, 2010

Key words: graft copolymers; irradiation; polysaccharides

INTRODUCTION

Cassia plants[1] are renewable reservoirs for nonconventional seed gums. *Cassia marginata* (CM)[2] *syn: Cassia roxburghii* is a large Indian tree with cylindrical and indehiscent long pods with a black cathartic pulp (which is used as a horse medicine) and polysaccharide-rich seeds. It has been reported[3,4] that vinyl grafting can induct favorable properties in the seed gums while retaining their favorable properties; for example, polyacrylamide (PAM)-grafted guar gum (GG) is used in the preparation of flocculants[5] and as a biodegradable drag-reducing agent.[6] Crosslinked guar-*graft*-PAM based crosslinked anionic microgels have been reported[7] as a pH-sensitive drug-delivery system. Various conventional redox systems[3,8,9] have been used to graft PAM onto GG; because of concurrent homopolymer formation, usually low grafting yields have been obtained. Microwave (MW) irradiation[10,11] is used for a variety of organic transformations,[12,13] including polymerization reactions,[14,15] wherein chemical reactions are accelerated because of the selective absorption of MW energy by polar molecules. Recently, vinyl monomers[16,17] have been grafted on polysaccharides in aqueous media without any catalyst or initiator. MW-promoted grafting, when done in the presence of a low concentration of potassium persulfate,[18] also furnishes a grafted product in good yield.

In recent years, solid supports,[19,20] such as montmorillonite clay, alumina, silica, alkali metal, fluoride-doped alumina, and commercial bentonitic earths, have been used to conduct reactions under MWs. Heterogeneous organic reactions, where reagents are immobilized on porous solid supports, have advantages over conventional, solution-phase reactions; these advantages include enhanced reaction rates, higher yields, greater selectivity, and ease of manipulation. The couplings of MW irradiation with the use of mineral supports under solvent-free conditions provide cleaner[20] chemical processes. The literature reveals that the solid-supported grafting of vinyl monomers on natural polymers has so far not been attempted, except in our previous study[21] on the alumina-supported grafting of acrylonitrile onto CM gum. To explore whether the solid-supported MW grafting method can be generalized with other monomers, in this study, we grafted acrylamide onto CM gum.

Seed gums isolated from different plant sources usually have different molecular weights and secondary structures;[22] therefore, different properties for *Cassia marginata* seed gum-*graft*-polyacrylamide (MWS-GP) were expected than for PAM-grafted

GG.[3,8,9] Because the CM seed gum was grafted with PAM for the first time, the properties of the graft copolymer were studied and compared with the parent CM gum to explore the possibility of its commercial exploitation as a flocculant[23,24] or hydrogel[25] in controlled drug release.[26,27] The properties of the saponified *Cassia marginata* seed gum-*graft*-polyacrylamide (SMWS-GP) were also studied, as PAM-grafted sodium alginate[28] showed better flocculation properties than sodium alginate itself. The properties of differently synthesized copolymers were also compared.

EXPERIMENTAL

A Kenstar domestic MW oven (Kolkata, India; model OM 20 ESP, 1000 W) with a MW frequency of 2450 MHz and a power output of 0–800 W with continuous adjustment was used for all of the experiments. Neutral alumina (Merck, India) was used as a solid support. CM seed gum was supplied by Himani Seed Stores (Deheradun, India) and identified by a systematic botanist at the Botanical Survey of India (Allahabad, India). Acrylamide (Merck, India) was recrystallized twice from methanol (Merck, India; Gravimetric Reagent (GR)) and dried *in vacuo*; ascorbic acid and potassium persulfate (Merck, India, analar grade) were used without further purification. The viscosity measurements were done on a Brookfield viscometer (model LVDVE, Brookfield Engineering Laboratories, Lorch, Germany) with a small sample adapter (spindle no S-18) at 30°C. IR spectra were recorded on a Fourier transform infrared (FTIR) spectrophotometer (model Nicolet 5700; CNR IMM, Bologna) with KBr pellets. Solid-state ^{13}C-NMR studies were done on a Fourier transform NMR spectrometer (model DSX-300-MHz for solids, Bruker, Bruker BioSpin GmbH, Germany). X-ray diffraction (XRD) was carried out on an X-ray diffractometer (model D8, Bruker AXS, Inc., WI), and thermogravimetric analysis (TGA) was done in an N_2 atmosphere (model Mettler Toledo STARe, Mettler-Toledo, Inc., Columbus, OH). Gas liquid chromatography (GLC) was performed with a gas chromatograph equipped with a flame ionization detector at 190° with a Superleco S P 2380 column (3.0 × 0.53 mm), with the carrier gas being nitrogen (model Neukon 5700, Nucon Engineers, New Delhi, India). A sample with a maximum level of percentage grafting was used for the characterization by spectral studies. The efficiency of grafting (%E) was the criteria for optimization of the grafting conditions.

Isolation and purification of the seed gum

Dried, crushed seeds after successive extraction[1] with light petroleum and ethanol (for defatting and decolorizing, respectively) were extracted with 1% aqueous acetic acid, and the extract was added slowly with stirring to a large excess of ethanol. The crude gum was collected, washed with ethanol, dried (yield = 3.0 g/100 g), and purified[1] through barium complexing. The pure seed gum was a nonreducing white amorphous material with an ash content of 0.28% and $[\alpha]_D^{25}$ of +57° (water).

Hydrolysis of the seed gum

The pure seed gum was completely hydrolyzed with 1M trifluoroacetic acid (4 h at 100°C). The identities and configurations of the constituent monosaccharides were confirmed by cochromatography of the hydrolyzate with authentic samples and by the preparation of derivatives. The ratio of the constituent monosaccharides was determined by GLC.[29]

Graft copolymerization

Alumina-supported grafting under MW irradiation (without initiator)

CM seed gum (0.1 g) was dissolved in the minimum required amount of water (3 mL) and mixed thoroughly with 0.2 g of neutral alumina and a known amount (2.95 × 10^{-3} M) of acrylamide. The slurry was exposed to different MW powers for definite time periods. After exposure, the reaction mixtures were stirred well in water with a magnetic stirrer and filtered, whereupon the solid support was separated. The filtrate was precipitated in methanol–water (7 : 3) to obtain the graft copolymer. The maximum level of grafting (%G) was obtained at 480 W of MW power in 50 s. The grafted MWS-GP was repeatedly washed with methanol–water (7 : 3) to get rid of any adhered homopolymer and dried. %G and %E were calculated as follows[29]:

$$\%G = \frac{W_1 - W_0}{W_0} \times 100\% \tag{1}$$

$$\%E = \frac{W_1 - W_0}{W_2} \times 100\% \tag{2}$$

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

The experiment was repeated at various concentrations of monomer (1.41 × 10^{-3} to 4.22 × 10^{-3} M) at 480 W of power with 0.1 g of CM gum, 0.2 g of alumina support, and 50 s of exposure (the conditions at which 3.52 × 10^{-3} M acrylamide gave the optimum yield). At the optimum monomer concentration (3.52 × 10^{-3} M), MW power (480 W), and exposure time (50 s), the CM gum-to-alumina ratio was varied. The optimum %G was obtained with a

gum-to-alumina mass ratio of 1 : 6 (0.05 g of CM gum was impregnated on 0.3 g of alumina). The maximum %G and %E achieved were 288 and 57%, respectively Under optimum conditions, the reaction was repeated with hydroquinone (HQ; 20 mg) and also on the recovered alumina support.

Grafting under MW irradiation in aqueous media

To a solution of CM seed gum (0.05 g/25 mL), acrylamide (3.52×10^{-3} M) was added, and the reaction mixture was irradiated in a domestic MW oven in a 150-mL flask at 480 W of MW power for 50 s. The reaction product [the copolymer synthesized under MWs in aqueous media (MWA-GP)] was precipitated in methanol–water (7 : 3) as discussed previously, and %G and %E were 132 and 26%, respectively.

Alumina-supported grafting under MW irradiation (with initiator)

CM gum (0.05 g) was dissolved in the minimum required amount of water (3 mL) and mixed thoroughly with neutral alumina (0.3 g), acrylamide (3.52×10^{-3} M), ascorbic acid (2.3×10^{-2} M), and $K_2S_2O_8$ (10×10^{-3} M). The slurry was exposed to 480 W of MW power for 50 s. The reaction mixture was stirred well with water with a magnetic stirrer and filtered, whereupon the solid support was separated from the reaction mixture. The precipitation of the reaction mixture in methanol–water (7 : 3) furnished no precipitate.

Conventional grafting with the $K_2S_2O_8$/ascorbic acid redox pair in the thermostatic water bath

To a solution of CM gum (0.05 g in 25 mL) taken in a 150-mL reaction flask, acrylamide (3.52×10^{-3} M) and ascorbic acid (2.3×10^{-2} M) were added and thermostated in a water bath at $35 \pm 2°C$. After 30 min, $K_2S_2O_8$ (10×10^{-3} M) was added, and this time of addition of persulfate was taken as time zero. The graft copolymerization[4] was allowed to continue for 1 h. Then, the reaction product [the conventionally synthesized copolymer (Cv-GP)] was precipitated in methanol–water (7 : 3) as described previously; %G and %E were 200 and 20%, respectively.

Determination of the water and saline retention

An accurately weighed amount of the dried polymer (0.5 g) was placed in a previously dried and weighed sintered glass crucible (G-4), which was then filled with 100 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[29] per gram of the dried material, and this was taken as the water-retention capacity. Similarly, the saline-retention capacity was determined with 100 mL of a 1% aqueous sodium chloride solution.

Hydrolysis in aqueous alkali

Grafted CM gum samples (2 g on a dry basis) were hydrolyzed[29] for 3 h in 150 mL of 1% NaOH to get saponified graft copolymers. The hydrolyzates were then precipitated in 600 mL of methanol, washed with methanol and ethanol, dried, and weighed.

Viscosity measurements

To prepare[29] the gum solutions, weighed quantities of the gum and grafted gums were dissolved separately in required quantities of water to obtain the desired concentrations (1–2% w/v). The solutions were agitated vigorously for about 15 min until they were viscous and homogeneous.

Gel formation

Gels[30] were prepared by the addition of a known amount of borax as the solid to 8 mL of solution of the gum (1% w/v)/grafted gum (2% w/v); this was followed by shaking. The time required for gel formation with different amounts of borax and the viscosities of the resulting gels were measured.

RESULTS AND DISCUSSION

Cassia plants in general are reported to possess seed galactomannans,[31] which have a linear chain of $\beta(1\rightarrow4)$-linked D-mannopyranosyl units, to which D-galactopyranosyl side chains are attached through $\alpha(1\rightarrow6)$ linkages. The galactose-to-mannose ratio in galactomannans sourced from different plants varies. In CM seed gum, the galactose-to-mannose ratio was detected[30] to be 1 : 2.5 by GLC, as compared to 1 : 2 reported[1] in GG. Different molecular weights of the two seed gums are evident by their viscosities. The viscosity of a 1% CM gum solution (w/v) was measured to be 768 cP, which was significantly less than the reported[1] viscosity of a 1% GG solution (1340 cP); this indicates that CM gum has a lower molecular weight.

In the alumina-supported, MW-induced grafting method, the maximum %G and %E achieved were 288 and 57%, respectively, with 3.52×10^{-3} M acrylamide, 0.05 g of CM seed gum, 0.3 g of alumina support, and 50 s of exposure to 480 W of MW power. The mass ratio of CM gum to alumina was 1 : 6. %G and %E in this study were much higher than those of the polyacrylonitrile grafting on CM gum

TABLE I
%G and %E of the Alumina and Recovered Alumina Support with 3.52×10^{-3} M Acrylamide, 50 mg of CM Seed Gum, 300 mg of Alumina Support, 480 W of MW Power, and 50 s of Exposure

Sample no.	Alumina support	Alumina recovered at each stage (%)	%G	%E
1	Alumina	—	288	57.6
2	Recovered alumina, first cycle	93	280	56
3	Recovered alumina, second cycle	93	250	50
4	Recovered alumina, third cycle	93	240	48

reported in our previous study, where a %G of 186% with a %E of 77% were achieved with 4.56×10^{-3} M acrylonitrile, 0.1 g of CM gum, 0.3 mg of alumina support, and 80 min of exposure to 640 W of MW power. This difference may have been due to the different monomer types used and the different gum-to-alumina ratios used in the two studies, but it was evident that the method was fairly applicable for both of the monomers.

Quenching of the grafting in the presence of a little HQ indicated the participation of free radicals in the grafting process.

After each cycle, 93.3% of the alumina support could be recovered, and the reaction was found to be reproducible on the recovered alumina (Table I). When reused, the recovered alumina, even in the third cycle, resulted in a %G of 240% and a %E of 48%, which were still higher than the %G and %E obtained in $K_2S_2O_8$/ascorbic acid initiated conventional grafting (%G = 200% and %E = 40%) and MW-promoted aqueous grafting (%G = 132%; %E = 26%) at an identical monomer concentration (Table II). Because, on recycling, the efficiency of the solid support did not lose much, the use of a solid support in the copolymer synthesis did not add much to the cost.

As under the influence of MWs, the grafting was feasible even in the absence of a radical initiator or catalyst, we concluded that the MW irradiation significantly accelerated the grafting reaction. The use of the solid support in the MW-promoted grafting procedure further enhanced the yield; this has been reported in other solid-supported reactions. The better %G and %E values in the solid-supported grafting compared to aqueous MW grafting could be explained because the reagents immobilized on the porous solid supports such as alumina had a better opportunity to interact. A drastic reduction in the reaction time and improved yield were observed because of the rapid heating ability of the solid support under MWs,[32] which, in turn, transferred energy to the reactants for faster reaction rates and improved yields.

When the $K_2S_2O_8$/ascorbic acid redox initiator was used in the alumina-supported MW grafting, no grafting was observed; instead, on MW exposure, the reaction mixture turned brown and purple at the walls of the reaction vessel. Although the full understanding of this observation requires more investigations, we assumed that, under MW, the redox initiator generated radicals very quickly, and these radicals, instead of initiating grafting, decomposed the seed gum to furfural derivatives.

Formation of the free radicals without initiator under MW irradiation

A free-radical mechanism for the grafting was most probable, as the grafting was not observed in the presence of a radical scavenger (HQ). Because no radical initiator was added from outside, the free radicals generated due to the MW dielectric heating (resulting from the localized rotation of the pendant hydroxyl groups[10] at the polysaccharide molecule under the influence of the MWs) were responsible for the observed grafting. Further, MW have also been reported to have the special effect[11] of lowering the Gibbs energy of activation of reactions. In view of these two effects, a plausible free-radical mechanism for the grafting under MW irradiation is proposed. The OH groups at CM gum, being most polar, absorbed the MW energy and cleaved, generating monomer free radicals, which initiated the graft copolymerization.

When HQ was added to the reaction vessel, no grafting was observed. It reacted with the radicals available in the reaction medium to terminate chain propagation and itself converted to an HQ radical, which, being stable, was unable to initiate polymerization (Scheme 1).

TABLE II
%G and %E in Various Grafting Procedures at Optimum Monomer Concentration

| Sample no.	Grafting method	Copolymer sample	Medium	%G	%E
1	Aqueous thermal grafting (with $K_2S_2O_8$/ascorbic acid)	Cv-GP	Aqueous	200	40
2	MW-promoted aqueous grafting (without initiators)	MWA-GP	Aqueous	132	26
3	MW-promoted alumina-supported grafting (without initiators)	MWS-GP	Dry medium	288	57
4	MW-promoted alumina-supported grafting (with initiators)	—	Dry medium	—	—
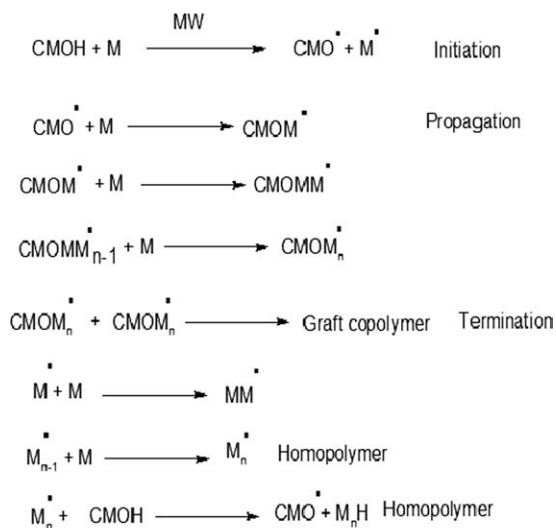
Scheme 1 Mechanism of grafting of acrylamide on the CM seed gum under MW power.

Optimization of the grafting conditions

Various reaction parameters were varied to optimize the MW-promoted, solid-supported grafting (the basis for the optimization was %E).

Effects of the MW power and exposure time

We studied the effects of the MW power and exposure time by impregnating 2.95×10^{-3} M acrylamide and 0.1 g of gum on 0.2 g of alumina support. Grafting was found to increase with increasing MW power up to 480 W. With increasing MW power, more MW energy was absorbed; this generated more macroradicals, which resulted a higher grafting yield. However, decreases in %G and %E were
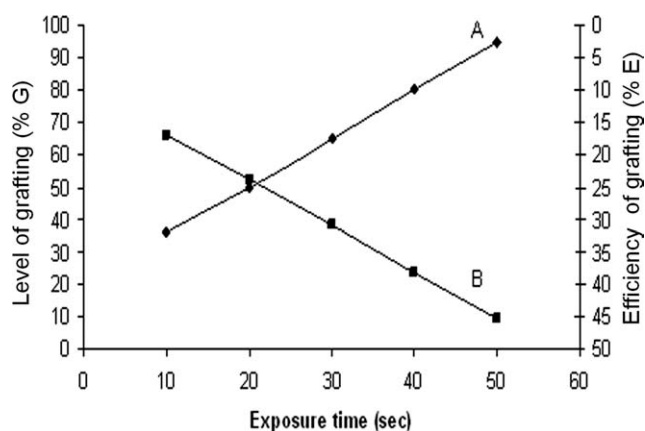
Figure 1 %G and %E at different exposure times with 480 W of MW power and 2.95×10^{-3} M acrylamide, 0.1 g of gum, and 0.2 g of alumina support.
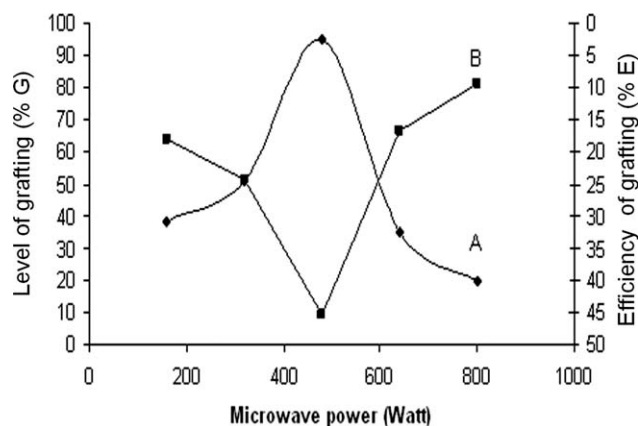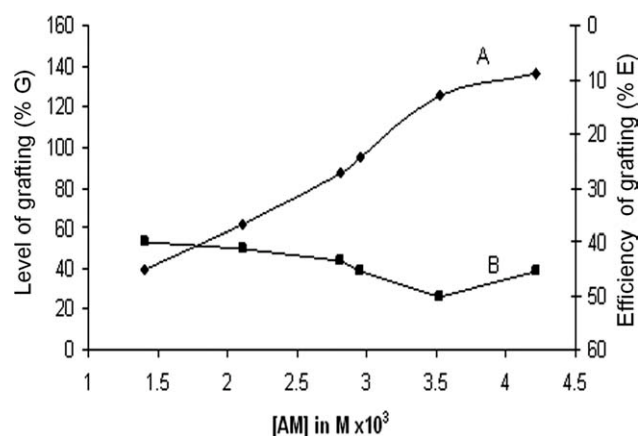
Figure 2 %G and %E at different MW powers at 50 s of exposure at an acrylamide concentration of 2.95×10^{-3} M, 0.1 g of gum, and 0.2 g of alumina support.

observed at MW powers greater than 480 W (Fig. 1). At a fixed MW power (480 W), the yield increased initially with increasing exposure time but decreased when the sample was exposed for more than 50 s (Fig. 2). The lower yield at high MW power and longer exposure time may have been due to the decomposition of the copolymer and, in part, to higher temperatures, which inhibited the free-radical reaction.

Monomer effect

The monomer concentration was varied from 1.41×10^{-3} to 4.22×10^{-3} M at 0.05 g of CM gum, 0.2 g of alumina support, 480 W of MW power, and 50 s exposure. The optimum %G was obtained with 3.52×10^{-3} M acrylamide. Increases in the monomer concentration beyond this point promoted more homopolymerization because of the decreased polysaccharide-to-monomer ratio, and thus, both %G and %E decreased (Fig. 3).

Figure 3 %G and %E at different acrylamide (AM) concentrations at 480 W of MW power, 50 s of exposure, 0.05 g of CM gum, and 0.2 g of alumina support.
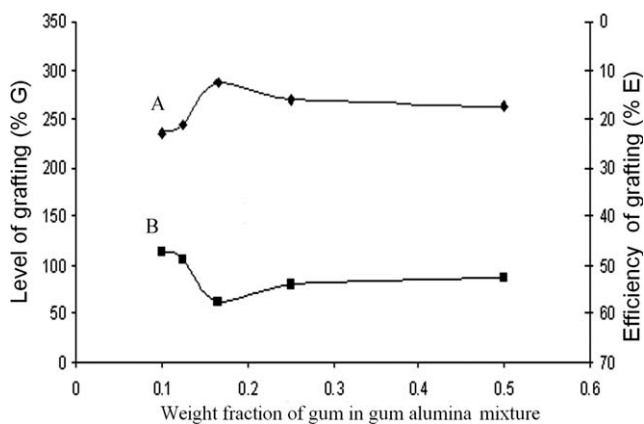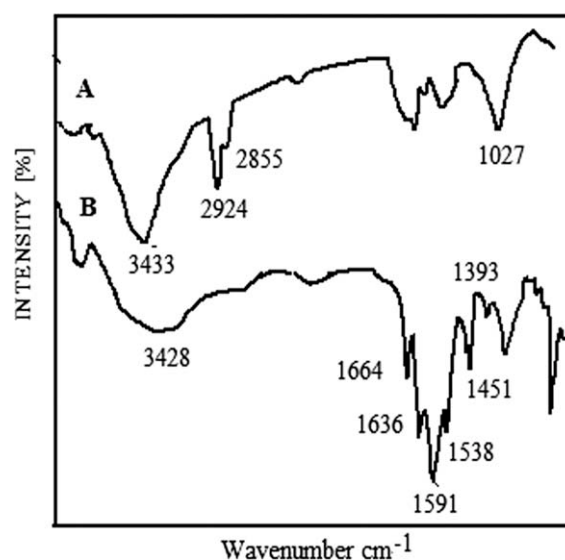
Figure 4 %G and %E at different weight fractions of gum in a gum–alumina mixture at 480 W of MW power, 50 s of exposure, and a concentration of 3.52×10^{-3} M of acrylamide.

Figure 5 IR spectra of (A) CM gum and (B) CM-*g*-PAM.

Effect of the seed gum-to-alumina ratio

On decreasing seed gum-to-solid support ratio (0.5–0.166) at 3.52×10^{-3} M acrylamide, 480 W of power, and 50 s of exposure, the grafting yield increased because a higher content of solid support (in the reaction mixture) offered a better interface for the reaction. Further decreases in this ratio decreased %G, as the excess of support resulted in poor interaction between the CM gum and monomer. Moreover, a decrease in the gum amount also decreased the gum-to-monomer ratio, which decreased the grafting yield (Fig. 4).

The CM seed gum was most efficiently grafted with 0.05 g of CM, 3.52×10^{-3} M acrylamide, 480 W of MW power, an exposure time of 50 s, and 0.3 g of solid support.

Characterization of the grafted gum

MWS-GP was characterized with FTIR spectroscopy (Fig. 5), ^{13}C-NMR (Fig. 6), XRD (Fig. 7), and TGA (Fig. 8) with CM gum as a reference.

FTIR

In FTIR spectrum of MWS-GP, N—H and O—H stretching absorptions were observed as a merged strong peak around 3428 cm.$^{-1}$ Amide I and II bands were present at 1664 and 1636 cm^{-1}, respectively. Aliphatic C—H stretching vibrations were seen at 2926 and 2856 cm^{-1}, whereas —CH$_2$ scissoring vibrations were observed at 1451 cm^{-1}. In CM gum, however, amide I and II vibrations were not seen. The presence of the N—H and C=O stretching
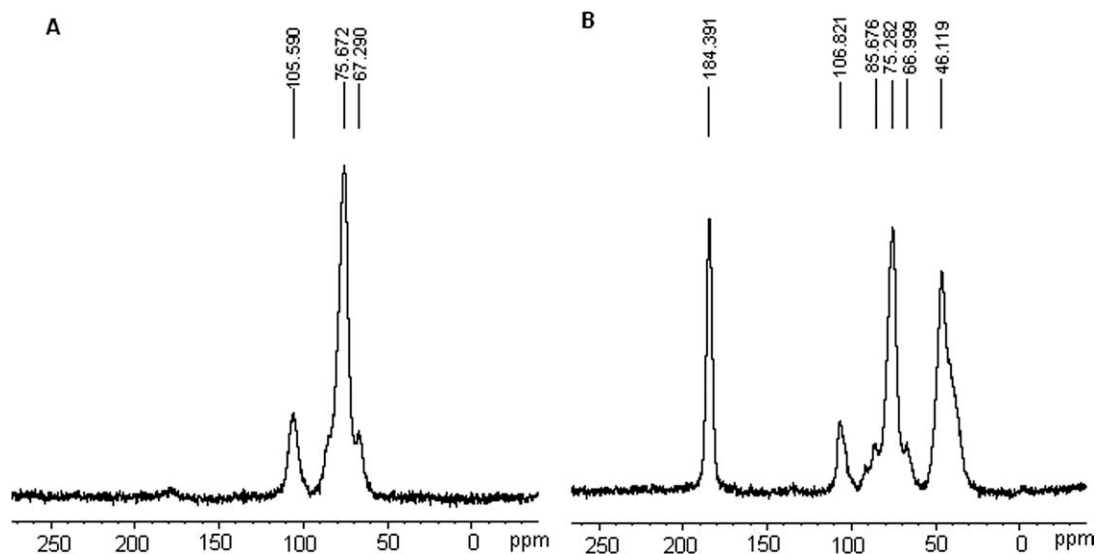
Figure 6 Solid-state ^{13}C-NMR spectra of (A) CM gum and (B) GC (MWS-GP).
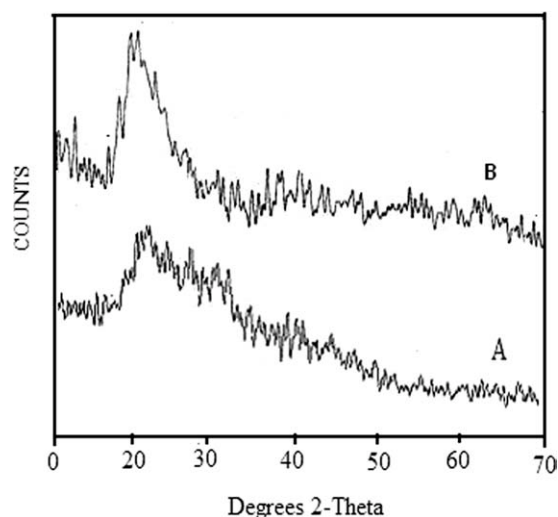
Figure 7 XRD patterns of (A) CM gum and (B) MWS-GP.

vibrations in the graft copolymer confirmed the grafting (Fig. 5). The physical blend of CM gum and PAM after the selective removal of PAM with methanol–water (7 : 3) showed no absorption due to N—H and C=O stretching. This substantiated the formation of the graft copolymer.

^{13}C-NMR

In the ^{13}C-NMR spectrum of CM gum [Fig. 6(A)], anomeric carbons were observed at 105.590 ppm, whereas other saccharide carbons were observed between 60 and 85 ppm. In the graft copolymer MWS-GP [Fig. 6(B)], additional peaks at 184.391 ppm (due to amide carbonyl carbons) and at 40–50 ppm (due to methylene carbons and carbons connected to the carbonyl carbons of amide) were observed, which confirmed the grafting of PAM onto the CM gum backbone.
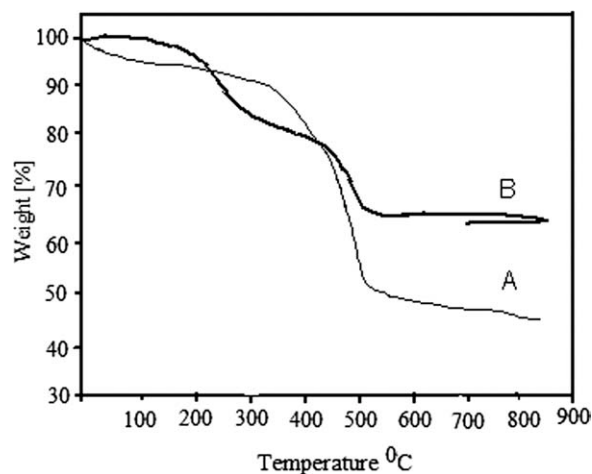
Figure 8 TGA thermograms of (A) CM gum and (B) MWS-GP.

TABLE III
Water, Saline Retention, and Viscosity of the 1% Solutions (w/v) of the CM Seed Gum and MWS-GP

Sample no.	Sample	Water retention (g/g of sample)	Saline retention (g/g of sample)	Viscosity (cP) at 0.5 rpm
1	CM gum	32.15	18.4	978
2	Cv-GP	17.1	10.9	1158
3	MWA-GP	18.8	12.7	1032
4	MWS-GP	11.0	6.8	2424
5	SMWS-GP	31.0	23.4	3594
6	SMWA-GP	24.2	14.5	1986
7	SCv-GP	25.6	17.8	2316

XRD

The XRD spectrum of CM gum showed a hallow typical of the amorphous structure, whereas in MWS-GP, the hallow sharpened in the region 2θ 20–22° because of the presence of PAM grafts at the CM seed gum. The change in the XRD pattern also confirmed the grafting (Fig. 7).

TGA

TGA of the CM gum showed a 5% weight loss up to 150°C due to the loss of adhered and bound water; then, there was a second weight loss (~ 57%), which was slow up to 300°C and was followed by a sharp loss up to 500°C due to the loss of the polysaccharide, whereas the graft copolymer MWS-GP showed thermal stability with only a 40% weight loss up to 700°C. Weight loss in MWS-GP took place in two stages; the first sharp weight loss was between 200 and 450°C due to the loss of the gum, whereas the second loss, between 450 and 500°C, was due the loss of graft chains in the copolymer. There was no loss up to 100°C in MWS-GP; this indicated that no water was adhered to it (Fig. 8).

Properties of the grafted gum

Water and saline retention

The water-retention properties were due to the interaction of the hydroxyl groups of the seed gums through hydrogen bonding. The grafting of the vinyl monomers onto the seed gum occurred through the hydroxyl groups[29] and was due to the lower availability of the hydroxyl groups. The water-retention capacity of the copolymer was less than that of the CM gum. This decrease in the water retention was found to be proportional to the grafting percentage in the samples. As at same monomer concentration, %G was higher in the MW-synthesized copolymer; water and saline retention by them were lower (Table III). On saponification, the increases in the

TABLE IV
Change in the Viscosities of 1% Solutions (w/v) of SMWS-GP, SMWA-GP and SCv-GP with Time (h) at 30°C at 0.6 rpm

Sample no.	Time (h)	Viscosity of CM		Viscosity of Cv-GP		MWS-CP		MWA-CP		Viscosity* (SMWS-GP)		Viscosity* (SMWA-GP)		Viscosity* (SCv-GP)	
		%T	(cP)	%T	(cP)	%T	(cP)	%T	(cP)	%T	(cP)	%T	(cP)	%T	(cP)
1	0	76.8	768	50.3	1006	96.8	1936	88.6	1772	61.9	3097	35.1	1775	45.9	2295
2	24	59	590	50.3	1006	96.8	1936	88.6	1772	75.2	3760	35.1	1775	45.9	2295
3	36	52	520	50.3	1006	96.8	1936	88.6	1772	75	3790	35.1	1775	45.9	2295
4	48	49.5	495	50.3	1006	96.8	1936	88.6	1772	77	3850	35.1	1775	45.9	2295
5	72	23.6	236	50.3	1006	96.8	1936	88.6	1772	77	3850	35.1	1775	45.9	2295
6	96	16	160	50.3	1006	96.8	1936	88.6	1772	77	3850	35.1	1775	45.9	2295
7	120	16	160	50.3	1006	96.8	1936	88.6	1772	77	3850	35.1	1775	50.0	2205
8	144	—	—	50.3	1006	96.8	1936	88.6	1772	75	3750	35.1	1670	79	1938

RPM: CM = 3; Cv-GP = 1.5; MWS-GP = 1.5; MWA-GP = 1.5; SMWS-GP, SMWA-GP, and SCv-GP = 0.6.
%T, % Torque.

water- and saline-retention capacities of the copolymer were explainable as —$CONH_2$ groups being hydrolyzed to —COOH groups.

Viscosity

The conventionally synthesized gum had a lower viscosity compared to the MW-synthesized gum because of the lower %G in the latter. Because of the presence of PAM grafts, the viscosity of the grafted gum solutions were higher than the parent CM gum (Table IV). The viscosity of the MW-synthesized graft copolymer remained stable up to 168 h, and thereafter, biodegradation started, and the viscosity was then slowly lost, whereas the native seed gum was very sensitive to biodegradation, and its degradation started within 24 h. In SMWS-GP and the saponified copolymer synthesized under MWs in aqueous media (SMWA-GP), this degradation started after 144 h (Table V), whereas the viscosity of the saponified conventionally synthesized copolymer (SCv-GP) was stable up to 120 h. The presence of the PAM grafts in the copolymer was responsible for the higher shelf life of the grafted gum, which,

TABLE V
Gel Formation in CM (1% w/v) Gum/Grafted CM Gums Solutions (2 % w/v) with Borax (0.0125 g/8 mL)

| Sample no.	Gum	Time (min)	Viscosity (cP) at 0.3 rpm
1	CM gum	0.96	>10,000
2	Cv-GP	2.38	>10,000
3	MWS-GP[a]	1.70	>10,000
4	MWA-GP	1.93	>10,000
3	SMWS-GP	3.46	>10,000
4	SMWA-GP	0.98	>10,000
5	SCv-GP	1.86	>10,000

[a] No gel formation with 0.0125 g of borax/8 mL gum solution; gel formation occurred with 0.015 g of borax/8 mL gum solution.

on saponification, hydrolyzed to poly(acrylic acid) (Scheme 2 and Tables IV and V).

Because the viscosities of the grafted CM gum and its saponified derivatives were stable up to 144 h, they may be useful in the production of biodegradable, drag-reducing agents.[33]

Gel formation

Hydrogels[34] are significantly important in tissue engineering and find use as matrices for repairing and regenerating a wide variety of tissues and organs. Therefore, the gelling behavior of the seed gum and grafted gums were studied to assess their potential use as hydrogels. CM gum had numerous adjacent hydroxyl groups in the cis arrangement, and thus, on addition of borax, it was capable of giving a three-dimensional gel. On grafting, some of the —OH groups of the seed gum were substituted with PAM, and the available *cis*-OH groups for the interaction with the gelling agent decreased. Thus, for gel formation of the grafted gums, a higher concentration of the gelling agent was required (Table V). Eight milliliters of each of the 2% (w/v) solutions of Cv-GP, MWS-GP, and MWA-GP was gelled in 2.38, 1.70, and 1.93 min, respectively, with 100, 120, and 100 mg of borax, respectively, whereas SCv-GP, SMWS-GP, and SMWA-GP were gelled in 1.86, 3.46, and 0.98 min, respectively, with 100 mg of borax; this indicated that the copolymers with higher %G values required more time to gel.
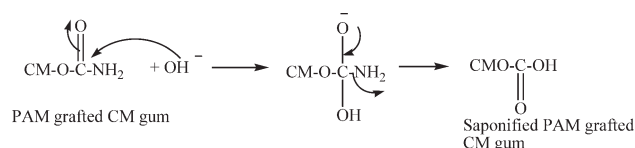
Scheme 2 Saponification of PAM grafts on the CM gum backbone, where CM stands for CM seed gum.

CONCLUSIONS

MWS-GP was synthesized very efficiently without any radical initiator or catalyst in a very short reaction time with 480 W of MW power on a neutral alumina support. The %G and %E obtained in the alumina-supported grafting under MWs were much higher than those obtained in the MW-promoted aqueous grafting and persulfate/ascorbic acid initiated thermal grafting at same monomer concentration. Grafted CM gum had a lower water/saline retention than native CM gum, and a 1% solution of the MWS-GP solution had a medium-range viscosity that was stable to biodegradation up to 168 h. Both the CM gum and PAM-grafted gum samples formed hydrogels with borax, although the grafted polysaccharide required more time to gel.

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