Ceric Ammonium Sulfate/Sodium Disulfite Initiated Grafting of Acrylamide on to *Cassia reticulata* Seed Gum

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ABSTRACT: Ceric ammonium sulfate/sodium disulfite redox system was evaluated for the poly(acrylamide) (PAM) grafting on to *Cassia reticulata* (CR) seed gum. Grafting conditions were optimized and the maximum %Grafting (%*G*) and %Efficiency (%*E*) achieved were 152 and 97.2%, respectively, using [disulfite] 0.005*M*; [ceric ammonium sulfate] 0.026*M*; [acrylamide] 0.11*M*; [gum] 0.125 g/25mL at 40 ± 0.2°C. Representative CR-grafted gum (CRPAM) was characterized by Fourier transform infrared spectrometry (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). Under identical conditions, the redox initiator could result 142.6 %*G* and 91.2 %*E* on to guar gum (GG). Various physical properties of the CR gum/grafted CR gum, such as viscosity, water retention, and saline retention, were studied and compared with GG/grafted GG to find out the potential industrial use of CR gum and PAM-*grafted*-CR gum. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1477–1484, 2008

Key words: *Cassia reticulata*; acrylamide grafting; ceric ammonium sulfate/sodium disulfite redox system

INTRODUCTION

The *Cassia reticulata* (CR) plant[1] is a small tree and commonly known as the Golden Lantern. It is cultivated in the tropical zones of India, but it easily grows in containers indoors at northern climates. The oil from its seeds is effective for the treatment of arthritis. Seed gums from Cassia plants in general are reported[2–4] to be nonionic, branched chain polymer consisting of straight chain of mannose units joined by β-D (1→4) linkages having α-D-galactopyranosyl units as side chain like guar gum (GG).

GG is used[5] as a viscosity builder and water binder in many industries like mining, textile, explosive, paper, petroleum, etc., but is rarely used in its natural form because of quick biodegradation.[6] In their natural form, seed gums are prone to biodegradation, while they turn stable[7] after grafting of the vinyl monomers. Grafting with vinyl monomers is the route for modifying the properties of the naturally occurring seed gums for their better industrial exploitation. Recently, our group reported that the Ipomoea plant seed gums after grafting[6] with acrylonitrile develops interesting properties, and the properties of the grafted gums depend on the extent of grafting that varies with fine structure of the seed gums.

Sanghi and coworkers[8] have found that poly (acrylamide) (PAM)-grafted-seed gums exhibit better flocculating characteristics than the conventional polysaccharides[9] alone and some of the synthetic polymer-based flocculating agents. Chemically modified guar GG-*g*-PAM-based crosslinked anionic microgels have been used as pH-sensitive drug delivery systems.[10] GG grafted with PAM is a good shear stable drag reducing agent.[11]

Ceric ion,[12] redox initiators,[6,13–15] γ-radiation,[16] and microwave irradiation[17–19] have been employed for the initiating graft copolymerization of vinyl monomers with the natural polysaccharides. Use of ceric(IV) ion alone has limitation of producing large quantities of the homopolymer; however, ceric ammonium sulfate/dextrose,[20] ceric ammonium nitrate-/nitric acid,[21] Ce(IV)/H_2SO_4 medium,[22] and peroxydiphosphate/disulfite[23] have been reported for efficient grafting. This article, for the first time, reports the use of ceric ammonium sulfate/sodium disufite redox pair for PAM grafting on to CR seed gum, in which significantly high %*G* and %*E* were observed. Grafting conditions for PAM grafting on to CR gum were optimized, and under similar conditions, the system was also evaluated for PAM grafting on to GG, in which %*G* and %*E* comparable with the CR gum were observed. Since CR has been grafted with PAM for the first time, the properties of PAM-*grafted*-CR gum have been studied and

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compared with the parent CR seed gum, GG, and grafted GG to explore the possibility of its commercial utilization.

EXPERIMENTAL

CR seeds were supplied by Himani Seed Stores (Dehradun, India) and were identified by the Botanical Survey of India, Allahabad. Acrylamide (Merck, India) was recrystallized with methanol before use. Sodium disulfite and ceric ammonium sulfate (Merck) were used without further purification. IR spectra were recorded on a Bowmen ABB FTLA2000 Infrared spectrophotometer with ATR accessory using KBr pellets. Brookfield LVDVE viscometer with small sample adapter (using spindle no SC4-18) was used for the viscosity measurements. XRD was carried out on Isodebeyxlex 2002 X-ray powder diffractometer and TGA was done at Perkin–Elmer TGA-7 at a heating rate of 10°C/min under nitrogen atmosphere. IR, XRD, and TGA were done from the samples with maximum %*G*. GLC was done using a model Neukon 5700 gas chromatograph equipped with flame ionization detector at 190° with a Superleco S P 2380 column (3.0 mm × 0.53 mm), and the carrier gas being nitrogen.

Isolation of the seed gum

Ground seeds (1 kg)[6] of CR were exhaustively extracted with petroleum ether (40–60°) in a Soxhlet followed by refluxing with 95% EtOH to defat and decolorize, respectively, and then suspended in 1% aqueous AcOH overnight and filtered. The filtrate (mucilage) was precipitated with 95% EtOH to give a white fibrous product. The crude gum was collected, washed with ethanol, and dried.

Purification

The gum was purified[6] by barium complexing, by preparing 2.5% (w/v) solution of the gum by continuous stirring for 12 h at 60°C and precipitating with saturated barium hydroxide solution. The complex was separated by centrifugation and taken in 1*M* acetic acid, stirred for 8 h, centrifuged and precipitated with 95% ethanol and subsequently washed with 70, 80, 90, and 95% ethanol.

Complete hydrolysis and quantification of constituent monosaccharides

The pure seed gum was hydrolyzed[24] with 1*M* trifluoroacetic acid (4 h, at 100°C). Paper chromatograph (PC) (solvent-*n*-butanol: isopropanol: water) revealed the presence of galactose (R_f 0.15) and mannose (R_f 0.21). Configurations of the monosaccharides were confirmed by the preparation of derivatives: D-galactose phenyl hydrazone, mp 154°C; D-mannose phenyl hydrazone, mp 198°.

The ratio of the monosaccharides was determined by GLC. The complete hydrolyzate of the seed gum was evaporated, the residue was reduced with sodium borohydride, and the product was acetylated with pyridine/Ac_2O (1 : 1 v/v, 1 h at 100°). The resulting alditol acetates were analyzed by GLC. The ratio of D-galactose to D-mannose was found to be 1.00 : 1.78.

Graft copolymerization

Weighed amounts of purified CR gum and acrylamide were dissolved in 25 mL water in a two-necked flask, which was purged with purified nitrogen for about 30 min. Known amount of ceric ammonium sulfate and sodium disulfite were added to the reaction flask and this time was taken as zero time, and then the graft copolymerization[15] was carried out for the desired time. The CR gum-*g*-PAM (CRPAM) along with some quantity of PAM formed in the system was poured in a mixture of methanol and water (35 : 15 v/v) whereby the PAM completely dissolves. Grafted material was dried and weighed. The percentage and efficiency of grafting were calculated as given later.[14,15]

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

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

where, W_1, W_0, and W_2 denote the weight of the CRPAM gum, the weight of original CR gum, and the weight of the monomer used, respectively. Under the optimal grafting conditions for CR seed gum, GG was also grafted and the grafted GG (GGPAM) was separated. The results are summarized in Table I.

Determination of water and saline retention

Weighed amount[6] of the dried polymer was taken in a previously dried and weighed sintered glass crucible (G-4), which was then filled with 25 mL of water. Suction from a vacuum pump was applied after 30 min. 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, the saline retention capacity was determined by using 1% aqueous sodium chloride solution. Measurements were done with CR, GG, CRPAM, and GGPAM, and the results are summarized in Table I.

TABLE I
Properties of the CR and CRPAM

S. No	Polymer	Viscosity of 1% solution at 35°C		%*G*	%*E*	Water retention at in g/g at 35 °C	Saline retention in g/g at 35°C
		Viscosity (cP)	Shear rate (s^{-1})				
1	CR gum	490	0.792	152	97.18	20.4	18.8
2	CRPAM	510	0.792	–	–	9.4	6.8
3	Guar gum	1,250	0.792	142.5	96.01	21.8	14.2
4	GGPAM	1,840	0.792	–	–	10.2	7.3

Film formation

Films[6] were cast by simply allowing the water dispersion of the polymers to evaporate to dryness on glass plate.

Viscosity measurements

For preparing the gum solution, weighed quantity of the gum was dissolved in minimum quantity of water by socking overnight followed by stirring and then it was made up to a desired concentration and agitated vigorously for about 15 min till the solution became viscous and homogeneous. The measurements were made using small sample adapter (spindle no SC4-18; shear rate 1.32 N/s, where N is rpm) of Brookfield LVDVE viscometer at 35°C. Viscosities of CR gum, CRPAM, GG, and GGPAM were determined after different time intervals, and the results are summarized in Table II.

To 8 mL solution of the gum/grafted gum, borax solution of known concentration (2 mL) was added. Viscosity of the gum/grafted gum solution after borax addition was measured, and the results are summarized in Table III.

RESULTS AND DISCUSSION

Mechanism of grafting

The mechanism of grafting is suggested as follows: Sodium disulfite in aqueous medium react with water to give disulfite ion and that with ceric ions furnish primary free radicals[23] (Scheme 1), which abstracts H from the guar gum backbone to give the macroradical CRO. The macroradical CRO adds onto the acrylamide (M) generating a new radical CROM, and this chain will grow till it combines with other such chains to give a graft copolymer (Scheme 1).

Determination of optimal grafting conditions

To optimize the conditions for the grafting of PAM on to CR gum, the concentration of acrylamide, sodium disulfite, ceric ammonium sulfate, CR gum and the temperature were varied keeping grafting time and volume of the reaction mixture fixed at 1 h and 25 mL, respectively. The maximum %*G* and %*E* were found to be 152 and 97.2%, respectively.

Effect of sodium disulfite concentration

The %*G* and %*E* were increased with the increase in the disulfite concentration ranging from 0.006 to 0.05*M* and reached a maximum value at 0.05*M* at fixed concentration of acrylamide (0.07*M*), ceric ammonium sulfate (0.006*M*), and 0.1 g/25 mL gum at 40°C ± 0.2°C (Fig. 1). It may be due to the fact that at this concentration range, the activation along the backbone takes place immediately followed by the graft copolymerization of the monomer onto the

TABLE II
Viscosity of the Gums (c 1% w/v) and Grafted Gums (c 3% w/v) Aqueous Solutions on Addition of Borax at 30°C

S. No.	Gum/ grafted gum	Borax solution (c % w/v)	Viscosity in cP	
			Viscosity (cP)	Shear rate (s^{-1})
1	CR	1.25	7240	0.396
		2.50	9430	0.396
		5.00	Gels	–
		7.50	Gels	–
		10.0	Gels	–
		12.5	Gels	–
2	GCR	1.25	1632	1.32
		2.50	2757	1.32
		5.00	4475	0.792
		7.50	5850	0.66
		10.0	8940	0.396
		12.5	Gels	–
3	GG	1.25	Gels	–
		2.50	Gels	–
		5.00	Gels	–
		7.50	Gels	–
		10.0	Gels	–
		12.5	Gels	–
4	GGG	1.25	3895	0.792
		2.50	5262	0.66
		5.00	7310	0.396
		7.50	9730	0.396
		10.0	Gels	–
		12.5	Gels	–

TABLE III
Viscosities of the GG and CR Gum Measured by Brookfield Viscometer at Different Time Intervals

S. No.	Polymer		Viscosity in cP at different time intervals at 35°C (shear rate 0.792 s^{-1})							
			0 h	24 h	48 h	72 h	96 h	120 h	144 h	192 h
1.	CR	Viscos. in cP	490	360	325	300	278	205	170	150
2.	GG	Viscos. in cP	1250	1150	970	525	225	190	160	140
3.	CRPAM	Viscos. in cP	510	510	510	510	500	470	360	255
4.	GGPAM	Viscos. in cP	1840	1840	1840	1840	1800	1790	680	395

backbone. An increase in %*E* was observed with the increase in the concentration of disulfite.

Effect of ceric ammonium sulfate concentration

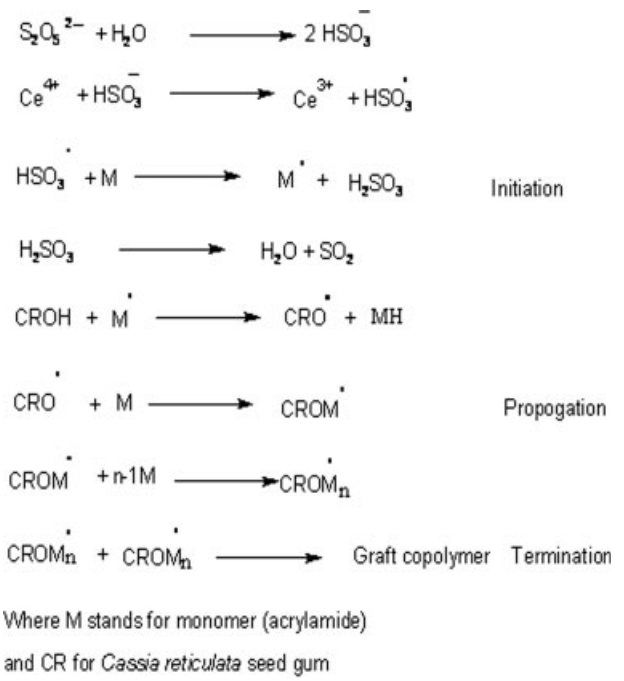
The effect of ceric ammonium sulfate was studied in the range 0.006–0.026*M* at fixed concentration of acrylamide (0.07*M*), sodium disulfite (0.05*M*), gum 0.1 g/25 mL at 40°C ± 0.2°C (Fig. 2). It was observed that both %*G* and %*E* increases with the increase in the concentration of ceric ammonium sulfate, which may be due to the generation of more primary free radicals that can generate more grafting sites.

Effect of monomer concentration

At the fixed concentration of ceric ammonium sulfate (0.026*M*), disulfite (0.05*M*), and CR gum (0.1 g/25 mL) at 40°C ± 0.2°C (Fig. 3), increase in the concentration of monomer from 0.07 to 0.15*M*, results in the increase in the %*G*. Although %*E* increases with the monomer concentration initially up to 0.11*M*, later it decreases. The increase in %*G* and %*E* may be due to the formation of more M_n while generating more grafting sites and availability of extra monomer for grafting. On increasing the concentration of the monomer beyond 0.11*M*, the %*E* decreases slightly, and this may be probably because of the homopolymer formation.

Effect of gum concentration

The effect of gum concentration was studied in the range of 0.05–0.150 g/25 mL at the fixed concentration of disulfite (0.05*M*), ceric ammonium sulfate (0.026*M*), acrylamide (0.11*M*) at 40°C ± 0.2°C (Fig. 4). It was found that %*E* increased up to 0.125 g/25 mL gum concentration (which may be due to the more availability of the macroradicals), thereafter decreases probably because of the increase in the viscosity of the reaction medium, which cause hindrance to the normal grafting reaction, and also because of the decrease in the monomer/polysaccharide ratio.



Scheme 1 Mechanism of grafting.

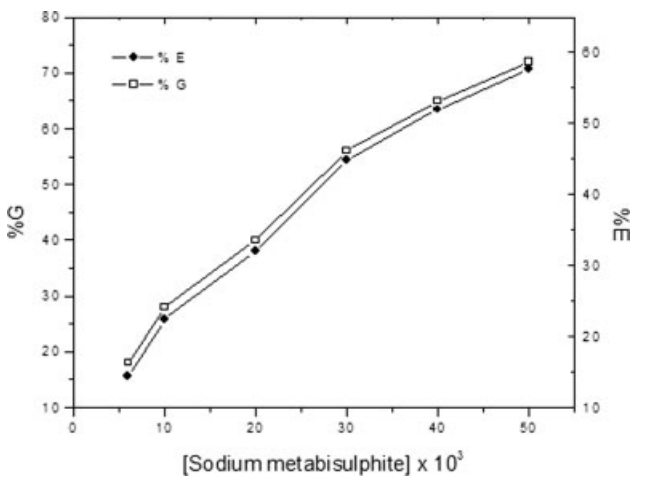


Figure 1 Effect of sodium disulfite concentration on %*G* and %*E*; [Acrylamide] 0.07*M*; [Ceric ammonium sulfate] 0.006*M*; [Gum] 0.1 g/25 mL at 40°C ± 0.2°C.

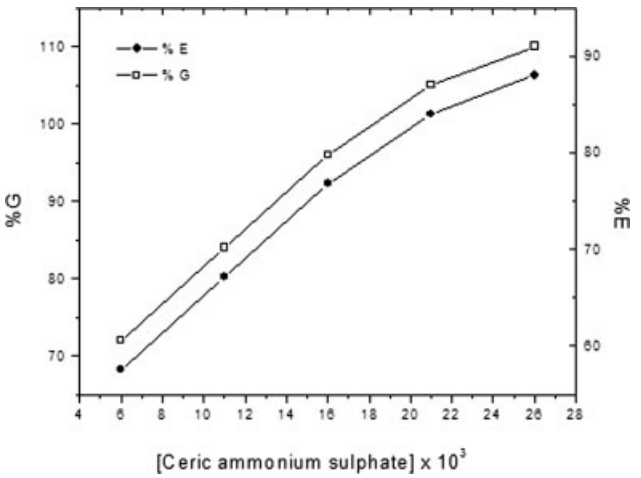


Figure 2 Effect of ceric ammonium sulfate concentration on %*G* and %*E*; [Acrylamide] 0.07*M*; [Sodium disulfite] 0.05*M*; [Gum] 0.1 g/25 mL at 40°C ± 0.2°C.

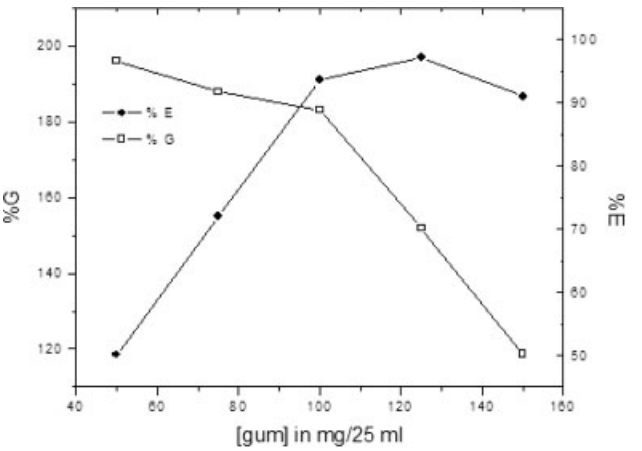


Figure 4 Effect of gum concentration on %*G* and %*E*; [Sodium disulfite] 0.05*M*; [Ceric ammonium sulfate] 0.026*M*; [Acrylamide] 0.11*M* at 40°C ± 0.2°C.

Effect of temperature

The grafting reaction was carried out at different temperatures (25–50°C) keeping other variables constant; [disufite] 0.05*M*; [ceric ammonium sulfate] 0.026*M*; [acrylamide] 0.11*M*, and [gum] 0.125 g/25mL (Fig. 5). Maximum %*G* was obtained at 40°C. The observed increase in %*G* with the increase in the temperature may be attributed to the increase in the number of collisions between the monomer and the gum molecules that results because of the decrease in the viscosity of the medium at higher temperature. Further increase in temperature decreases the %*G* and %*E*; this may be due to more homopolymerization at such temperatures.

Effect of grafting time

The grafting was done at different grafting time (15–75 min) keeping other variables constant; [disufite] 0.05*M*; [ceric ammonium sulfate] 0.026*M*; [acrylamide] 0.11*M*, and [gum] 0.125g/25 mL (Fig. 6). Maximum %*G* was obtained at 60 min. The %*G* increased rapidly with an increase in time up to 60 min after which it levels off. It could be attributed to a decrease in concentration for both initiator and monomer; thereby, there is a reduction in the number of sites on the backbone accessible for grafting as the reaction proceeds.

Overall maximum %*G* and %*E* that could be achieved were 152 and 97.2%, respectively, with [disulfite] 0.05*M*; [ceric ammonium sulfate] 0.026*M*; [acrylamide] 0.11*M*; [gum] 0.125 g/25 mL at 40°C.

Using the redox pair under identical grafting conditions, the guar gum could be grafted with 142.6

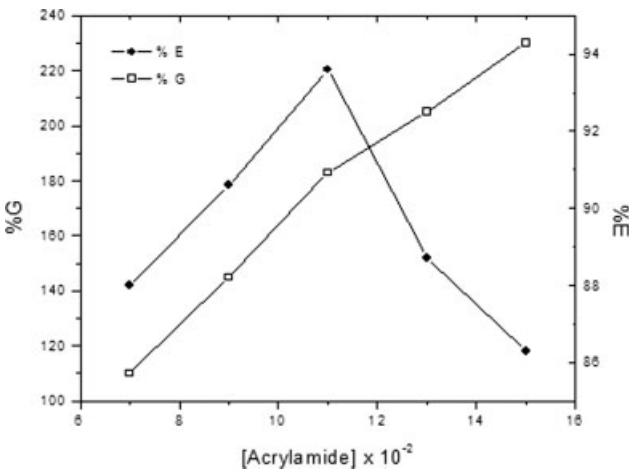


Figure 3 Effect of acrylamide concentration on %*G* and %*E*; [Sodium disulfite] 0.05*M*; [Ceric ammonium sulfate] 0.026*M*; [Gum] 0.1 g/25 mL at 40°C ± 0.2°C.

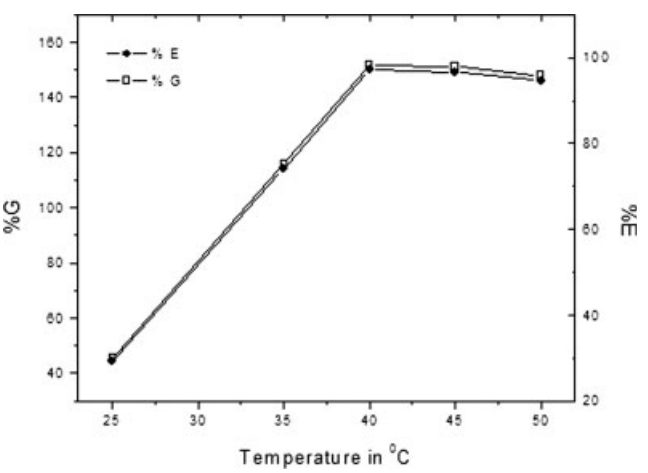


Figure 5 Effect of reaction temperature on %*G* and %*E*; [Sodium disulfite] 0.05*M*; [Ceric ammonium sulfate] 0.026*M*; [Acrylamide] 0.11*M*; [Gum] 0.125 g/25 mL.

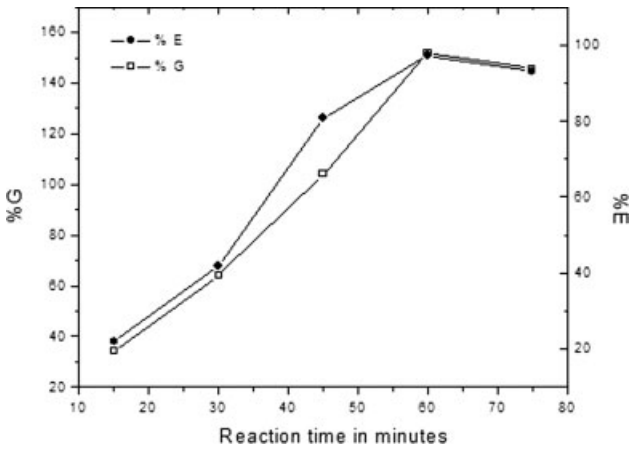


Figure 6 Effect of reaction temperature on %*G* and %*E*; [Sodium disulfite] 0.05*M*; [Ceric ammonium sulfate] 0.026*M*; [AA] 0.11*M*; [Gum] 0.125 g/25 mL.

%*G* and 91.2 %*E*. Thus it was observed that sodium disulfite/ceric ammonium sulfate redox system could be efficiently used to graft PAM on to CR gum and GG.

Viscosity

At 0.792 s^{-1} shear rate, viscosity of 1% solution of CR gum and CRPAM gum (%*E* 97.18) were found to be 490 and 510 cP, respectively, in comparison with 1250 and 1840 cP for GG and GGPAM (%*G* 91.15). The viscosity of the pure CR and GG gum solutions were found prone to biodegradation, and their viscosity started to degrade within 24 h on standing, whereas the grafted gum solutions were stable for 72 h and thereafter decrease slowly. Thus after grafting the viscosity, the shelf-life of the CR and GG gums increase significantly.

Because of the presence of numerous adjacent cis-hydroxyl groups, CR gum is capable of complexing with borax and therefore on addition of borax, the viscosity of the gum solution increases and at certain borax concentration, the gum solution gels. In the grafted gum, however, some of the —OH groups are replaced with PAM grafts and thus are not available for the complexing. Higher borax/gum concentration is therefore required to gel the grafted gum solution. The grafted gums did not give gel unless 3% solutions were used.

Films

Films formed by the pure seed gums are brittle and stick to the glass surface, the grafted gums formed films, which were flexible and could be easily peeled off from the glass surface.

Water and saline retention

The water and saline retention property is due to the interaction of the hydroxyl groups of the seed gums through hydrogen bonding. The grafting of the vinyl monomers onto the seed gums occurs through the hydroxyl groups at its backbone thereby

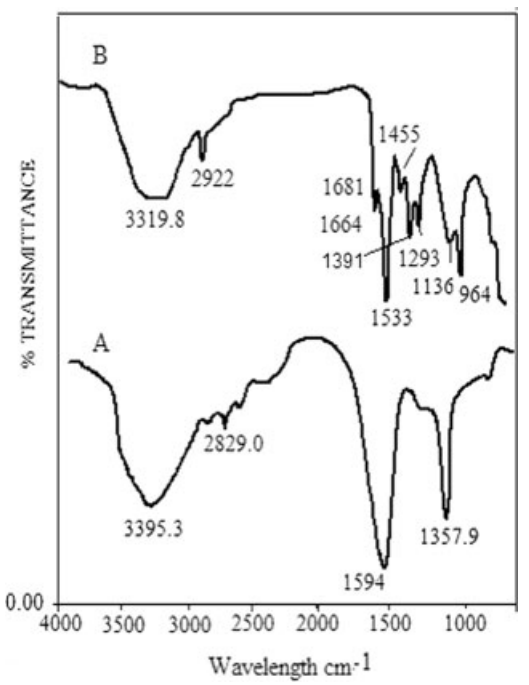


Figure 7 (A) IR Spectrum of CR and (B) IR spectrum of CR-*g*-PAM.

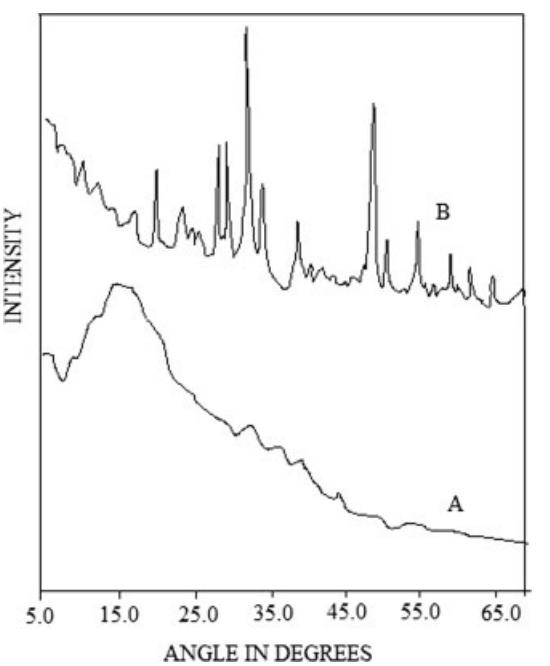


Figure 8 (A) XRD of CR gum and (B) XRD of CR-*g*-PAM.

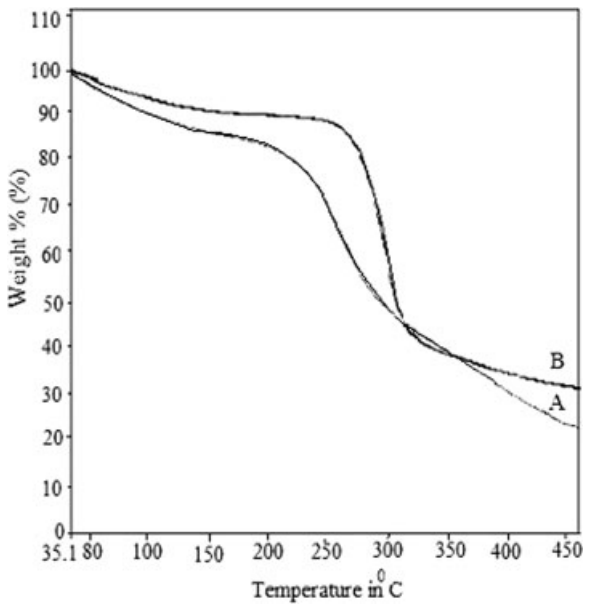


Figure 9 (A) TGA CR gum and (B) TGA of CR-*g*-PAM.

decreasing the number of the hydroxyl groups and consequently water/saline retention capacity of the grafted gums. Decrease in the water/saline retention has been observed to be proportional to the %*G*.

Characterization of the grafted gum

The representative CRPAM sample (sample with maximum %*E*) was characterized by XRD, IR, NMR, and TGA.

FTIR spectra

Infrared spectrum of pure CR gum has a broad strong band at 3395 cm^{-1}, a band at 2829 cm^{-1} indicating —OH group, C—H linkages, respectively, whereas IR spectrum of CR gum-*g*-PAM has amide I and amide II absorption bands at 1681.83 and 1664.45 cm^{-1}, respectively, C—H stretching at 2922 cm^{-1}, N—H stretching peaks at 3319 cm^{-1}, and C—N stretching at 1455 cm^{-1}. An intense peak of methylene C—H bending (of the grafted chains) at 1391 cm^{-1} further supports the grafting (Fig. 7). Physical blend of CR gum and PAM after selective removal of PAM with methanol : water (7 : 3) showed no absorption at 1664, 1455, and 3310 cm^{-1}. This substantiates the formation of the graft copolymer.

XRD

The XRD spectra of the pure CR gum shows amorphous nature, whereas in the XRD pattern of the grafted CR (Fig. 8) shows sharp crystalline peaks in the region of 2θ 18–20°, 25–35°, 37–40°, 48–50°, and 54–55° because of the incorporation of PAM grafts at the CR seed gum after grafting.

TGA spectra

The TGA of the pure gum shows that weight loss onsets at 244°C and a total weight loss of 65% up to 500°C, whereas in the grafted gum (Fig. 9), the decomposition onsets at 250°C and only 23% weight loss up to 500°C was observed, indicating that the grafted CR gum has high thermal stability as compared with the parent gum. The change in TGA curves clearly gave the grafting evidence.

CONCLUSIONS

Using ceric ammonium sulfate/disulfite redox system, grafting of PAM on to CR gum was found to be optimum at [disulfite] 0.005*M*; [ceric ammonium sulfate] 0.026*M*; [acrylamide] 0.11*M*; [gum] 0.125 g/25 mL at 40°C ± 0.2°C. Under identical conditions, GG could also be grafted efficiently using the system. Shelf lives of the grafted gum solutions were observed to be higher as compared with native gums. In conclusion, grafted gums from renewable plant sources like CR can be usefully exploited for various applications, and ceric ammonium sulfate/sodium disulfite redox system can efficiently graft the CR and the related gums.

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