Studies on $K_2S_2O_8$/Ascorbic Acid Initiated Synthesis of *Ipomoea dasysperma* Seed Gum-*g*-Poly(acrylonitrile): A Potential Industrial Gum

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ABSTRACT: Seed gum from *Ipomoea dasysperma* was grafted with polyacrylonitrile using potassium persulfate/ascorbic acid redox initiator in the presence of molecular oxygen, where the maximum percentage grafting and percentage efficiency observed were 360 and 97.2%, respectively. Optimal grafting conditions were established for the gum and a representative polyacrylonitrile grafted gum was characterized using FTIR, NMR, X-ray diffraction, and TGA studies. Grafted gums with %G up to 185% showed water solubility; thereafter, the solubility in water was observed to decrease with the increase in %G. After the saponification of the nitrile groups to amide and carboxylic acid groups, the water retention of the grafted gum increased significantly and this increase was dependent on the extent of grafting. Various properties like viscosity, gel/film forming ability, shelf life of the grafted gum solutions (with samples where %G were not >185%) along with the water, and saline retention capacity were studied and compared with that of the parent gum to evaluate it for industrial applications.
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Key words: Ipomoea *dasysperma* seed gum; grafting; polyacrylonitrile; properties

INTRODUCTION

Endosperms of Leguminous and Convolvulous plant seeds[1] provide a renewable reservoir of structurally different polysaccharides. Modifications of these naturally occurring polysaccharides by chemical means extend an excellent opportunity for the development of fine products for various industrial end applications.[2] Guar gum (GG), a seed gum from *Cyamopsis tetragonolobus*, forms highly viscous,[3] colloidal dispersions when hydrated in cold water. It is being used[4] as dispersions as a viscosity builder and water binder in many industries like mining textiles, explosives, paper, and petroleum. Although advantageous, this viscosity is difficult to control because of its quick biodegradation,[5] and that is why it is rarely used in its natural form. The viscosity of the gum solutions is reported to stablize[6] after vinyl monomer grafting. GG has been favorably modified by grafting various vinyl monomers using various redox systems[5,7] and microwave irradiation.[8,9] Singh and coworkers[10] have found that graft copolymers of guar/xanthan gum/starch exhibit much better flocculating characteristics than conventional polysaccharides[11] alone and some of the synthetic polymer-based flocculating agents. Lokhande et al.[12] prepared water supersorbent guar modified polymers by graft copolymerization of acrylonitrile onto it through γ radiations. Polyacrylamide grafted GG hydrogel microspheres[13] are used in water transport and drug release. Although grafted guar gum solutions have a better shelf life compared to guar itself, it cannot be used where low to medium viscous solutions are required as the grafted GG solution has very high viscosity.

A galactomannan[14] (Fig. 1) with significantly low viscosity compared to guar was isolated from the seeds of a widely distributed *Ipomoea dasysperma*[15] (ID) plant, which is found as wild vegetation in India. ID seed gum from a renewable plant source after grafting of vinyl monomers is expected to give grafted gum, which can furnish gum solutions of medium to low viscosity range with good shelf life. In this study, for the first time, polyacrylonitrile (PAN) was grafted onto ID seed gum and reaction conditions for the grafting were optimized using persulfate/ascorbic acid as a redox initiator. Under identical reaction conditions, the percentage grafting (%G) and percentage efficiency (%E) in ID gum were higher in comparison

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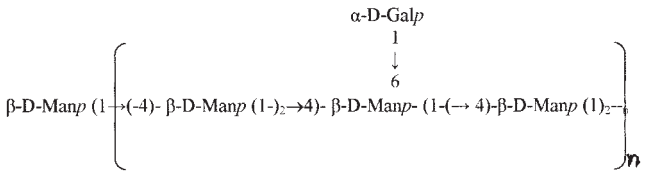


Figure 1 Structure[14] of the repeating unit of ID seed gum.

to GG. This grafted ID (IDAN) gum may find potential use in various industrial applications.

EXPERIMENTAL

ID seeds were supplied by Himani Seed Stores (Dehradun, India) and were identified by Botanical Survey of India, Allahabad. Acrylonitrile (Merck) was distilled in a stream of nitrogen before use. Ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification. Infrared (IR) spectra were recorded on a Brucker Vector-22 infrared spectrophotometer using KBr pellets. ^{1}H-NMR spectra were recorded on a Jeol 400-MHz FT NMR in D_2O. A Brookfield LVDVE viscometer with small sample adapter was used for the viscosity measurements. X-ray diffraction (XRD) was carried out on an Isodebeyxlex 2002 X-ray powder diffractometer and TGA was carried out on a Perkin-Elmer Pyris 6TGA in N_2 atmosphere. IR, XRD, NMR, and TGA were performed from the samples with 185%G. Viscosity and gel formation were also studied with the samples that were water soluble (%G 185%).

Isolation of the seed gums

Ground seeds[16] (1 kg) of ID 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) thus obtained 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[16] 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.

TABLE I
% G and % E in GG and ID gums (0.1 g) [Acrylonitrile] 0.26*M*, [Ascorbic Acid] 0.041*M*, [$K_2S_2O_8$] 0.05*M*; Total Volume 25 ml

			Temperature			
			35 ± 2 °C		60 ± 2 °C	
S.N.	Seed gum	Ratio Gal:Man	%G	%E	%G	%E
1	ID	1:6	331	89.3	360	93.4
2	GG	1:2	259	69.9	288	78.5

Graft copolymerization[5]

A calculated amount of the seed gum was dissolved in the minimum required amount of distilled water in a 150-mL flask. To this solution a calculated amount of the acrylonitrile and ascorbic acid were added and the total volume was made up to 25 mL, and the flask was thermostated at 35 ± 0.2 °C. After 30 min a definite amount of persulfate was added and this was taken as zero time (Table I). Grafting was allowed for 1 h and IDAN gum was separated from PAN (homopolymer) by pouring the reaction mixture into large quantity of dimethylformamide (DMF).[5]

The percentage and efficiency of grafting were calculated according to Kojima et al.,[17]

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

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

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

Determination of water and saline retention[5]

A weighed amount of the dried IDAN gum was taken in a previously dried and weighed sintered glass cru-

TABLE II
Water and Saline Retention for ID Gum, IDAN, and Alkali Hydrolyzed IDAN

S.N.	Gum	%G	Water retention (g/g)	Saline (1% NaCl) retention	Water retention of alkali hydrolyzed grafted gums (g/g)
1	ID	—	11.00	9.65	—
2	IDAN	80	3.50	2.60	18.20
		164	0.97	0.69	21.60
		185	0.88	0.63	27.90
		258	0.65	0.40	38.75

TABLE III
Gel Formation from ID Gum and IDAN

S.N.	Gum	Concentration in % (w/v)	Borax added (mg)	Time (s)	Viscosity of the gum solutions after borax addition (cP)
1	ID	1.0	125	39	2292
			250	24	4860
			500	14	> 10,000
2	IDAN	1.0	125	—	
			250	—	
			500	25	5050
			800	18	6800.
		2.0	650	42	> 10,000

cible (G-4), which was then filled with 50 mL of water. Suction from a vacuum pump was applied after 10 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, saline retention capacity was determined using 1% aqueous sodium chloride solution and the results are summarized in Table II.

Hydrolysis in aqueous alkali[18]

A total of 2 g of IDAN (on dry basis) was dispersed in 1% NaOH at 100 °C for 1.5 h. After hydrolysis the sample was precipitated in 600 mL methanol, washed with methanol followed by ethanol, dried, and weighed.

Water retention of the alkali hydrolyzed samples

A total of 0.5 g of the alkali-hydrolyzed IDAN (on dry basis) was swollen[18] in 100 mL distilled water for 10 min. The suspension was poured into a sintered glass filter (porosity 1) at 700 mm Hg pressure. The volume of the filtrate was measured and water retention was calculated as grams of water per gram of dry material (Table II).

Film[19]/gel formation[20]

Films were formed by simply allowing the water dispersion of the polymers to evaporate to dryness on a glass plate and gelling properties of the gum solutions were studied with borax. Results are summarized in Table III.

Viscosity measurements

To prepare the gum solution, a weighed quantity of the gum was dissolved in a 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 becomes viscous and homogeneous. The measurements were made using a small sample adapter (spindle No. *S*-18) of a Brookfield LVDVE viscometer at 30 °C. Viscosities of ID gum and IDAN (samples with different %G up to 185%) were determined after different time intervals and results are summarized in Table IV.

RESULTS AND DISCUSSIONS

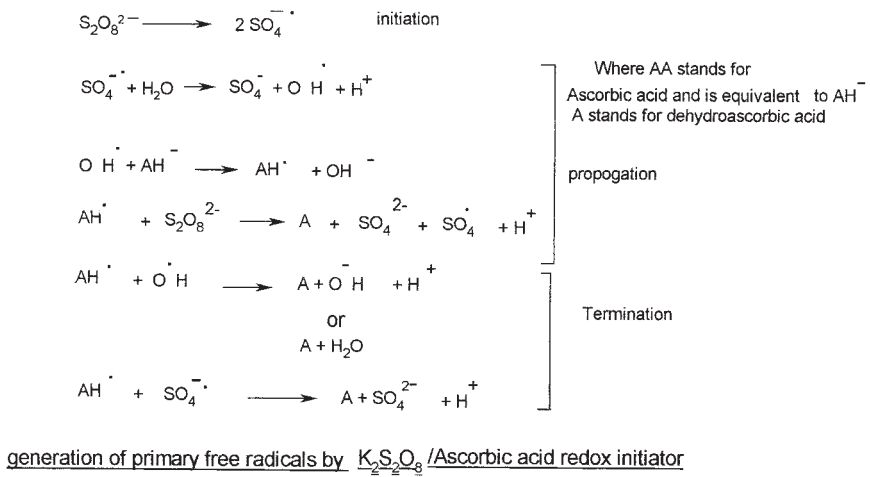
Mechanism of grafting

Mehrotra and Mushran[21] studied the kinetics of the redox system containing ascorbic acid and peroxydisulfate and a mechanism involving SO_4^{-}, $OH^{\cdot}$, and ascorbate radical intermediates has been proposed. This redox system has been exploited for polymerization of vinyl monomers by several workers[21,22] and has been shown to initiate vinyl copolymerization with guar gum.[5,7] The reaction between persulfate and ascorbic acid involves a chain mechanism[21] due to the formation of sulfate ion radicals, which are well-known ion chain carriers. The mechanism may be written as shown in Scheme 1.

SO_4^{-}, $OH^{\cdot}$, and $AH^{\cdot}$ (ascorbate radical) are the primary radicals, generated in the sequence of the redox reactions, and are expressed as $R^{\cdot}$ in the Scheme 2**.** They initiate the vinyl polymerization as the vinyl polymerization is reported to be faster than the H

TABLE IV
Viscosity of ID Gum and IDAN with % G and Time

			Viscosity of 1% gum solutions after different time intervals (cP)							
S.N.	Gum	%G	Initial	8 h	12 h	24 h	32 h	72 h	144 h	254 h
1	ID		3.87	3.87	3.48	3.20	2.43	2.25	2.23	—
2	IDAN	55	16.9	16.9	16.9	16.9	16.9	16.9	16.9	16.9
		80	40.9	40.9	40.9	40.9	40.9	40.9	40.9	40.9
		120	71.0	71.0	71.0	71.0	71.0	71.0	71.0	71.0
		140	78.6	78.6	78.6	78.6	78.6	78.6	78.6	78.6
		185	148.5	148.5	148.5	148.5	148.5	148.5	148.5	148.5



Scheme 1 Generations of primary free radicals by $K_2S_2O_8$/ascorbic acid redox initiator.

abstraction from the guar gum backbone. The macroradical IDO· may be generated by abstraction of H by the growing vinyl polymer radical, which may add onto the vinyl monomer (M), generating new radical IDOM·, and this chain will grow till it combines with other such chains to give a graft copolymer (Scheme 2).

Determination of optimal grafting conditions

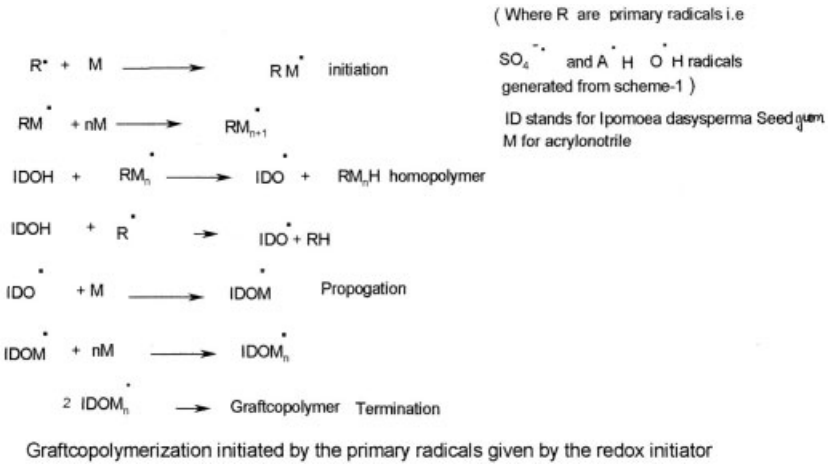
To optimize the condition for grafting of PAN on to the ID gum, the concentration of monomer, persulfate, and ascorbic acid, the weight of the gum, and the temperature were varied, keeping grafting time and total volume of the reaction mixture fixed at 1 h and 25 mL, respectively. The $K_2S_2O_8$/ascorbic acid redox system can be efficiently used to graft polyacrylonitrile onto ID gum where the maximum %G that could be achieved was 360%, and %E achieved was 97.2%.

Effect of monomer concentration

The increase in the concentration of monomer from 0.088 to 0.28*M* results in an increase of %G and %E (up to 0.17*M*) under the fixed concentration of 0.023*M* ascorbic acid, 0.01*M*. $K_2S_2O_8$, and gum 0.1 g/25 mL at 35 ± 0 2 °C (Fig. 2). 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. Upon increasing the concentration beyond 0.17*M* the %E decreases slightly; this may be due to homopolymer formation.

Effect of persulfate concentration

Percentage grafting increased with increase in initiator concentration and reached a maximum value at 0.05*M* persulfate at a fixed concentration of 0.28*M* acrylonitrile, 0.023*M* ascorbic acid, and 0.1 g/25 mL gum at 35 ± 0 2



Scheme 2 Graft copolymerization initiated by the primary radicals given by the redox initiator.

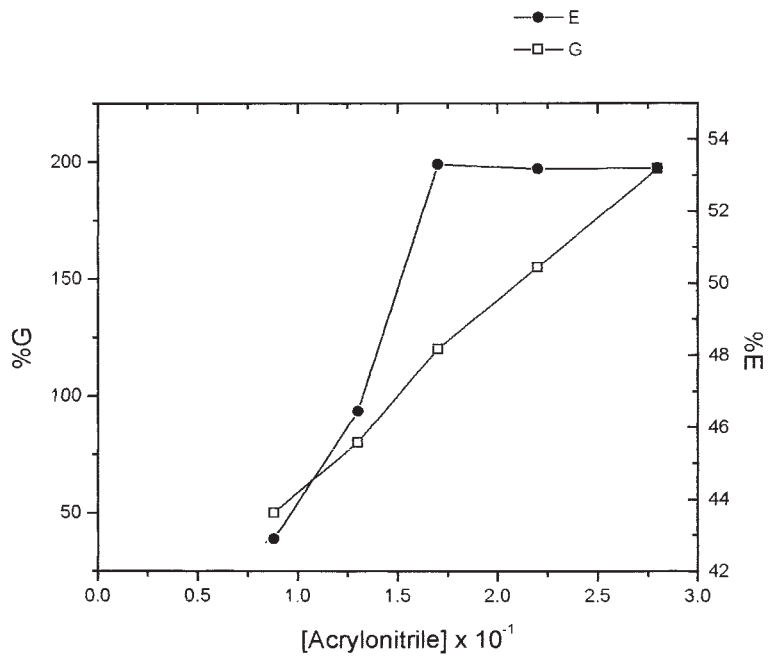


Figure 2 Effect of concentration of acrylonitrile on %G and %E; [$K_2S_2O_8$] 0.01*M*, [ascorbic acid] 0.023*M*; [gum] 0.1 g/25 mL at 35 ± 0 2 °C.

°C (Fig. 3). The observed increase in %G within the persulfate concentration ranging from 0.01 to 0.05*M* 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 back bone. An increase in %E was observed with the increase in the concentration of persulfate.

Effect of ascorbic acid concentration

The effect of ascorbic acid was studied in the range 0.023–0.041*M* at fixed concentration of 0.28*M* acrylonitrile, 0.05*M* potassium persulfate, and gum 0.1 g/25 mL at 35 ± 0 2 °C (Fig. 4). Both %G and %E increase with the increase in the concentration of ascorbic acid,

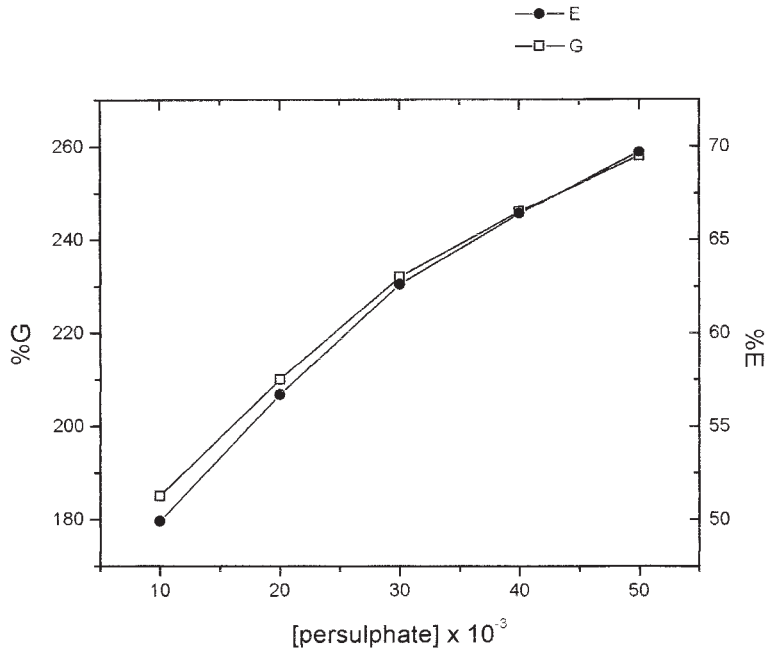


Figure 3 Effect of concentration of persulfate on %G and %E; [acrylonitrile] 0.28*M*; [ascorbic acid] 0.023*M*; [gum] 0.1 g/25 mL at 35 ± 0.2 °C.

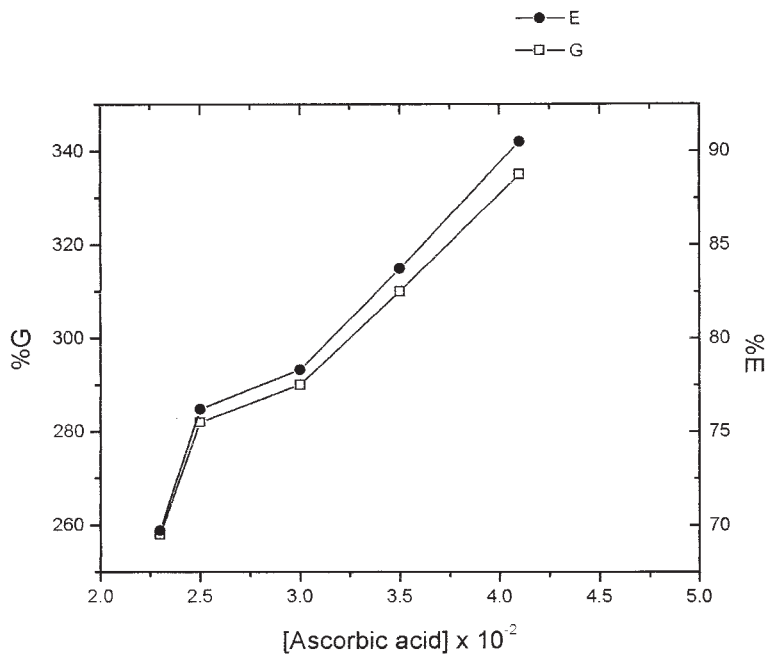


Figure 4 Effect of ascorbic acid concentration %G and %E; [persulfate] 0.05*M*; [acrylonitrile] 0.28*M*; [gum] 0.1 g/25 mL at 35 ± 0 2 °C.

which may be due to the generation of more primary free radicals, which can generate more grafting sites.

Effect of gum concentration

The effect of gum concentration was studied in the range of 0.1–0.3 g with the constant concentration of [persulfate] 0.05*M*, [ascorbic acid] 0.041*M*, and [acrylonitrile] 0.28*M* at 35 ± 0 2 °C (Fig. 5). Both %G and %E increased up to 0.15 g/25 mL gum concentration (which may be due to the greater availability of the macroradicals); thereafter, the %G and %E decrease, which may be due to the increase in the viscosity of the reaction medium causing hindrance of the normal reaction.

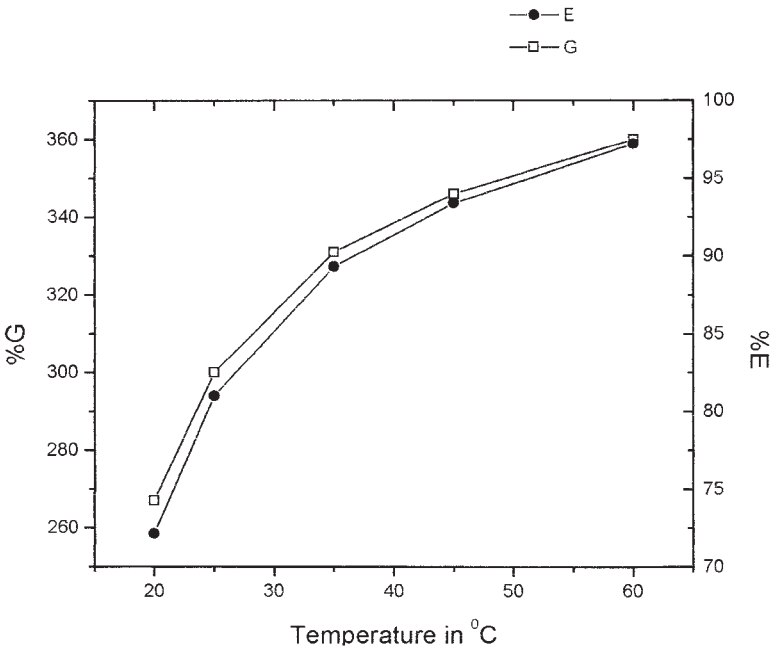


Figure 5 Effect of reaction temperature on %G and %E; [persulfate] 0.05*M*; [ascorbic acid] 0.041*M*; [AN] 0.28*M*; [Gum] 0.15 g/25 mL.

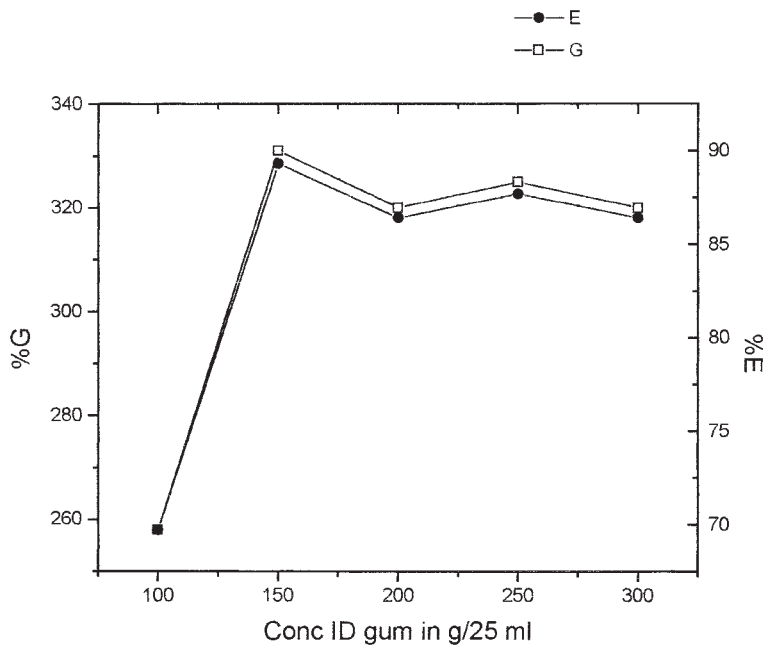


Figure 6 Effect of gum concentration on %G and %E; [persulfate] 0.05*M*, [ascorbic acid] 0.041*M*; [AN] 0.28*M* at 35 ± 0.2 °C.

Effect of temperature

The grafting reaction was carried out at different temperature (35–60 °C) keeping other variables constant; [persulfate] 0.05*M*; [ascorbic acid] 0.041*M*; [acrylonitrile] 0.28*M*, and [gum] 0.15 g/mL (Fig. 6). Maximum %G was obtained at 60 °C. The observed increase in %G may be attributed to the increase in the number of collisions between the monomer and the gum molecules that results due to decrease in the viscosity of the medium at higher temperature.

The overall maximum %G and %E that could be achieved was 360 and 97.2% with [persulfate] 0.05*M*, [ascorbic acid] 0.41*M*, [acrylonitrile] 0.28*M*, and [gum] 0.15 g/25 mL at 60°C. Due to fewer branched structures and less viscosity, ID seed gum was more efficiently grafted under similar grafting conditions in comparison to guar[4] that has greater branched structure. Higher branching and its high viscosity offer resistance in the grafting process.

Viscosity

The viscosity of 1% solution of ID gum was =3.87 cP, much less in comparison to guar, which is expected

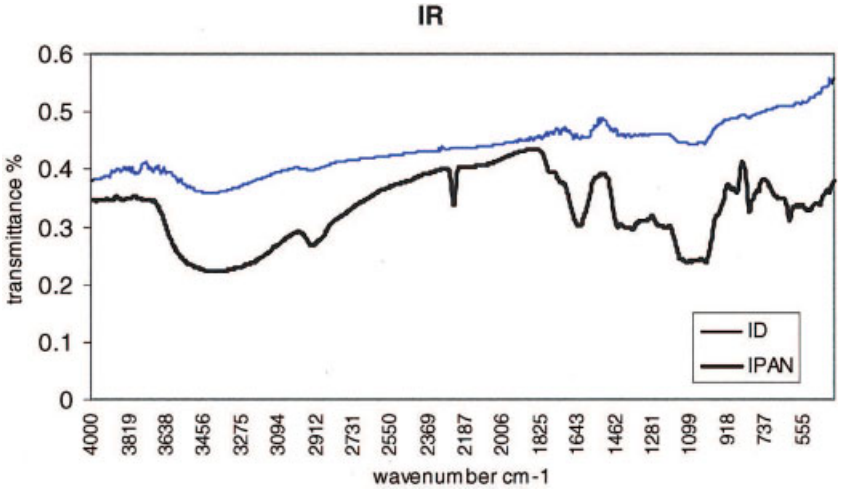


Figure 7 IR of ID and IDAN. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

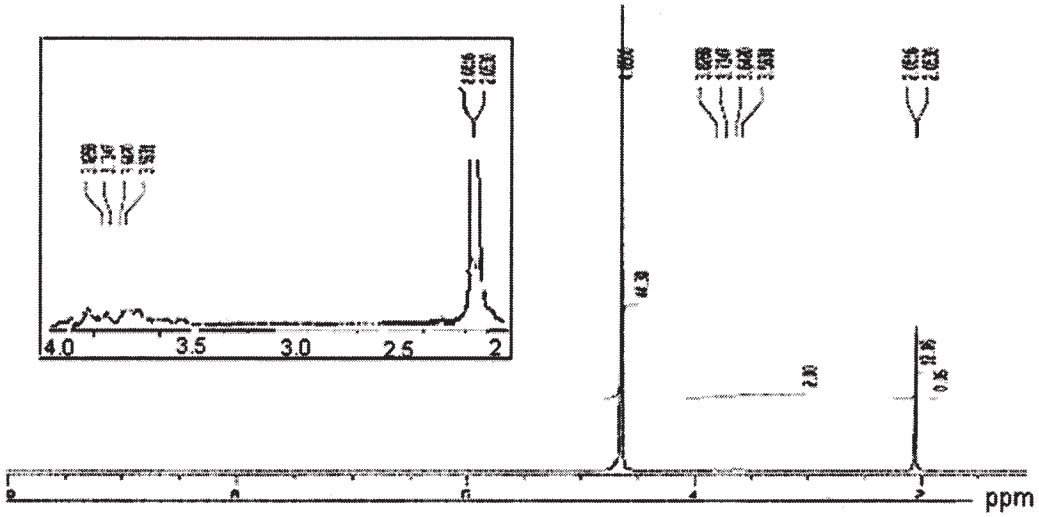


Figure 8 ^{1}H of ID gum.

because of its considerably less branched structural pattern and lower molecular weight compared to GG. The viscosity of the 1% IDAN gum (up to 185%G) solutions was studied and observed to increase with increase in %G (Table IV). The viscosity of the pure gum solution was prone to biodegradation and its viscosity was lost slowly on standing while the grafted gum solutions were found to retain their viscosity even after 254 h (Table IV). Thus, grafting results in increased viscosity and shelf life of the seed gum. However, the grafted samples with more than 185%G were not completely soluble in water.

Water retention

The water 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 of its backbone, thereby decreasing the number of the hydroxyl groups and consequently the water retention capacity of the grafted gum. A decrease in water retention has been observed to be proportional to the %G (Table II). On hydrolysis with aqueous alkali, the CN groups on the grafted chains get hydrolyzed to $-CONH_2$ and –COOH groups and this increases the extra water binding sites in the grafted gums and thereby a larger volume of water is bonded.

Gel/film

The gelling property of the gum is due to the interaction between the *cis* hydroxyl groups present on the

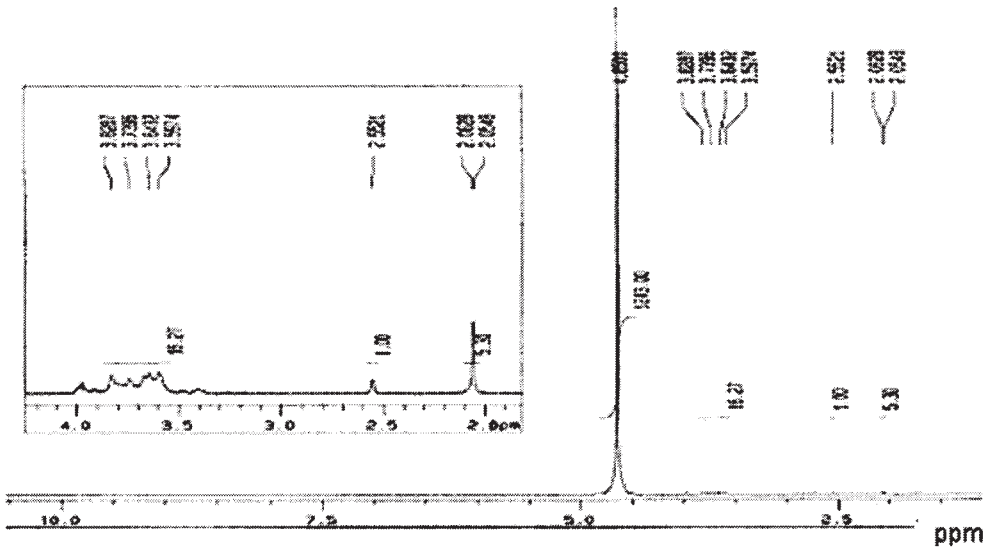


Figure 9 ^{1}H of IDAN.

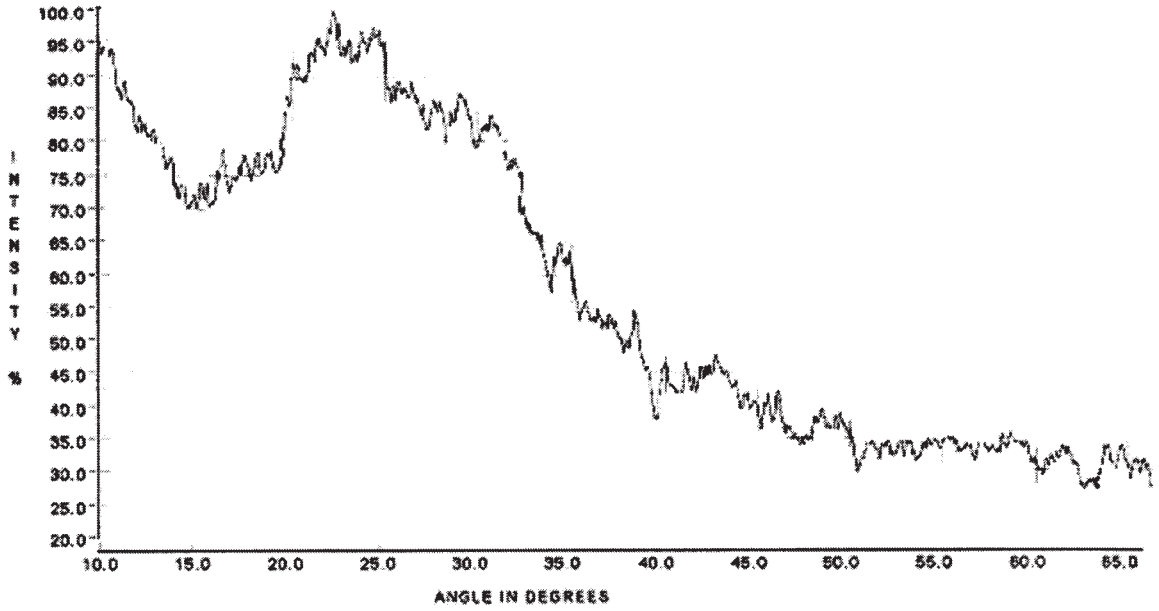


Figure 10 XRD of pure ID gum.

gum molecule and the borax. After grafting a smaller number of *cis*–OH groups are available for binding and therefore gel formation of the grafted gums requires higher gum concentration and a higher amount of the gelling agent compared to the parent gum. (Table III). While films formed by the pure seed gums are brittle and stick to the glass surface, the grafted gums form films that could be easily peeled off from the glass surface.

Characterization of the grafted gum

A representative IDAN sample (sample with maximum %G) was characterized by XRD, IR, NMR, and TGA.

The IR spectrum of pure ID gum has a broad strong band at 3313–3437 cm^{-1} and a band at 2900 cm^{-1}, indicating C-H linkages, while the IR spectra of IDAN (Fig. 7) had absorption peaks at 2243 cm^{-1} for –CN stretching and a CH_2 deformation vibration at 1410 cm^{-1}. Physical blends of gum and PAN after selective removal of PAN with DMF showed no absorption in the –CN stretching and -CH_2 bending region. This substantiates the formation of the graft copolymer.

^{1}H-NMR of the pure ID gum (Fig. 8) showed a peak at δ 4.65 (s) for anomeric protons and at δ 3.5–3.9 (m) and 2.05–2.06 (d) due to sugar protons, while the IDAN (Fig. 9) showed an additional peak at δ 2.5 (due to protons of methylene groups at

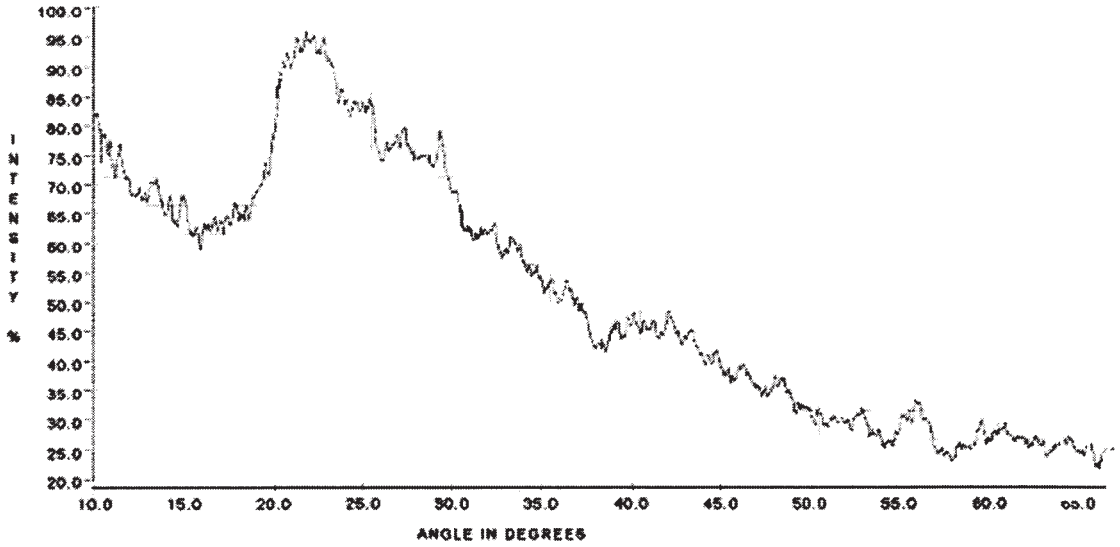


Figure 11 XRD of IDAN.

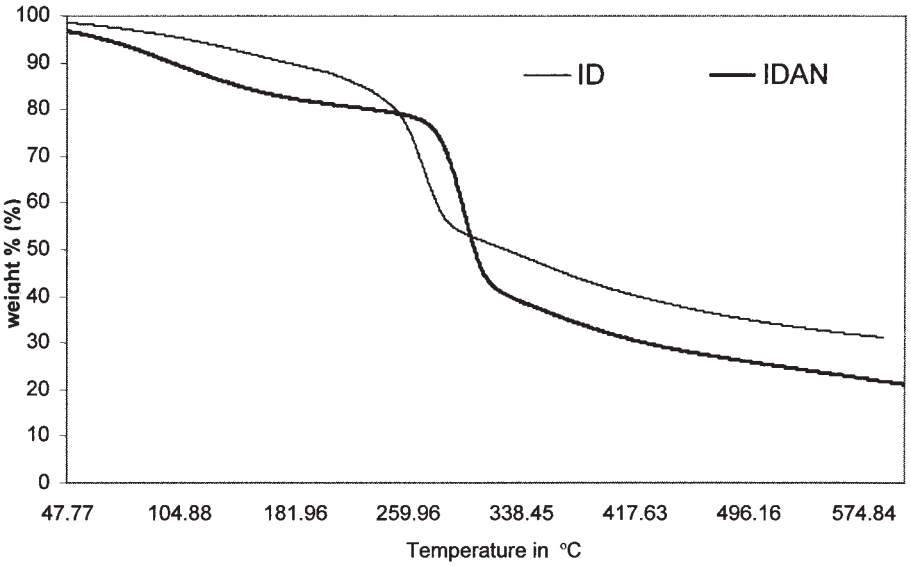


Figure 12 TGA of ID and IDAN.

grafted chains of PAN on the guar gum backbone), indicating the presence of PAN in the IDAN.

XRD of the ID and IDAN further supports grafting. (Fig. 10). The XRD spectra of the grafted gum showed increased crystallinity due to grafted PAN on the guar backbone in the region of 2θ 20–30° (Fig. 11).

TGA of the ID gum showed that decomposition begins at 228 °C while in IDAN it starts at 279 °C, indicating the grafted gum to be more thermally stable than the pure ID gum, but once the decomposition starts the weight loss is more rapid in IDAN than in pure ID gum (Fig. 12).

The extent of grafting of polyacrylonitrile chains and in turn the various physical properties of the grafted gums were dependent on the structural features of the natural seed gums (ID and GG in the present study) besides other reaction parameters. Thus, by grafting PAN on ID gum we obtain IDAN gum with properties different than GG–PAN.

CONCLUSIONS

Using a potassium persulfate/ascorbic acid redox system, grafting of acrylonitrile onto ID gum was optimum at [acrylonitrile] 0.28*M*; [$K_2S_2O_8$] 0.05*M*; [ascorbic acid] 0.41*M*; ID gum 0.15 g/25 mL at 60 ± 0 2 °C. Under similar grafting conditions, PAN could be grafted more efficiently onto the ID gum in comparison to guar. Viscosities of the grafted ID gum solutions were dependent on to the extent of the grafting and grafted gums up to 185%G were soluble in water. Solutions with medium to low viscosity range could be obtained from ID gum by changing the grafting conditions. In conclusion, grafted gums from renewable plant sources, like *I. dasysperma*, can be usefully exploited for various industrial applications.

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