

Polyacrylonitrile-Grafted *Cassia pudibunda* Seed Gum: A Potential Commercial Gum from Renewable Source

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ABSTRACT: *Cassia pudibunda* (CP) seed gum was grafted with poly(acrylonitrile) using persulphate/ascorbic acid redox initiator. Optimal grafting Conditions were determined and maximum % grafting and % efficiency observed were 294 and 85.3%, respectively. Grafted CP gum (gum-g-polyacrylonitrile; CP-g-PAN) was characterized using FTIR, XRD, and TGA analysis. The CP-g-PAN sample with maximum %G was observed to be water insoluble, however, 1% solution of the base-hydrolyzed CP-g-PAN had a viscosity of 114.7 centipoises, which was observed to increase continuously for first 5 days and there upon became fixed and was

shown to be stable even after 20 days when left at room temperature. Water and saline retention for CP-g-PAN after 10 min soaking were observed to be 47 and 30.15 g/g, respectively. Thus, base-hydrolyzed CP-g-PAN samples may find use as water sorbents and their aqueous solutions may be used commercially where medium to low viscosity solutions with high shelf life is the requirement. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 619–627, 2006

Key words: *Cassia pudibunda*; gum-graft-poly(acrylonitrile); potassium persulphate

INTRODUCTION

Endosperms of the Leguminous and Convolvulose plant seeds¹ in general provide a renewable reservoir of structurally different polysaccharides. *Cassia pudibunda* (CP) (N.O. leguminosae) is a shrub² and was found to be a rich source for the seed galactomannan like guar seeds.^{3,4} Guar gum has been modified for favorable properties by grafting vinyl monomers on to it using various redox systems^{5–9} and microwave irradiation.^{10–11} Cassia plants in general are reported^{12–15} sources for the seed gums having structure similar to guar gum, but in these nonconventional galactomannans, the ratio of the galactose to mannose and degree of branching are different and are found to vary from species to species. Recently, it was observed that under identical grafting conditions, the extent of the grafting and in turn the properties of the graft copolymers were dependent¹⁶ on the galactose to mannose ratio and the degree of the branching besides other grafting parameters. Owing to the tremendous application^{17–18} of the grafted gums and easy availability of the CP seed gum, the present study has been done to find out the possibility of exploiting it commercially and also to compare its grafting with guar gum in terms of %G, %E, and properties.

EXPERIMENTAL

The seeds of CP were supplied by Himani seed stores, Dehradun, India, and identified by Botanical Survey of India, Allahabad. Acrylonitrile (AN, Lancaster, synthesis grade) was distilled in a stream of nitrogen before use. Potassium persulphate (Merck) and ascorbic acid (AA; Loba) were used without further purification and double distilled water was used for the grafting reactions. FTIR spectra were recorded on a Bruker Vector-22 Infra red spectrophotometer using KBr pellets. X-ray diffraction (XRD) was carried out on Iodebexlex 2002 X-ray powder diffractometer and TGA was carried out on at Perkin–Elmer TGA-7 at a heating rate of 10°C/min under nitrogen atmosphere. 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 × 0.53 mm²), the carrier gas being nitrogen. For all the spectral studies and for water and saline retention, samples with maximum %G were used. The percentage and efficiency of grafting were calculated as follows:⁵

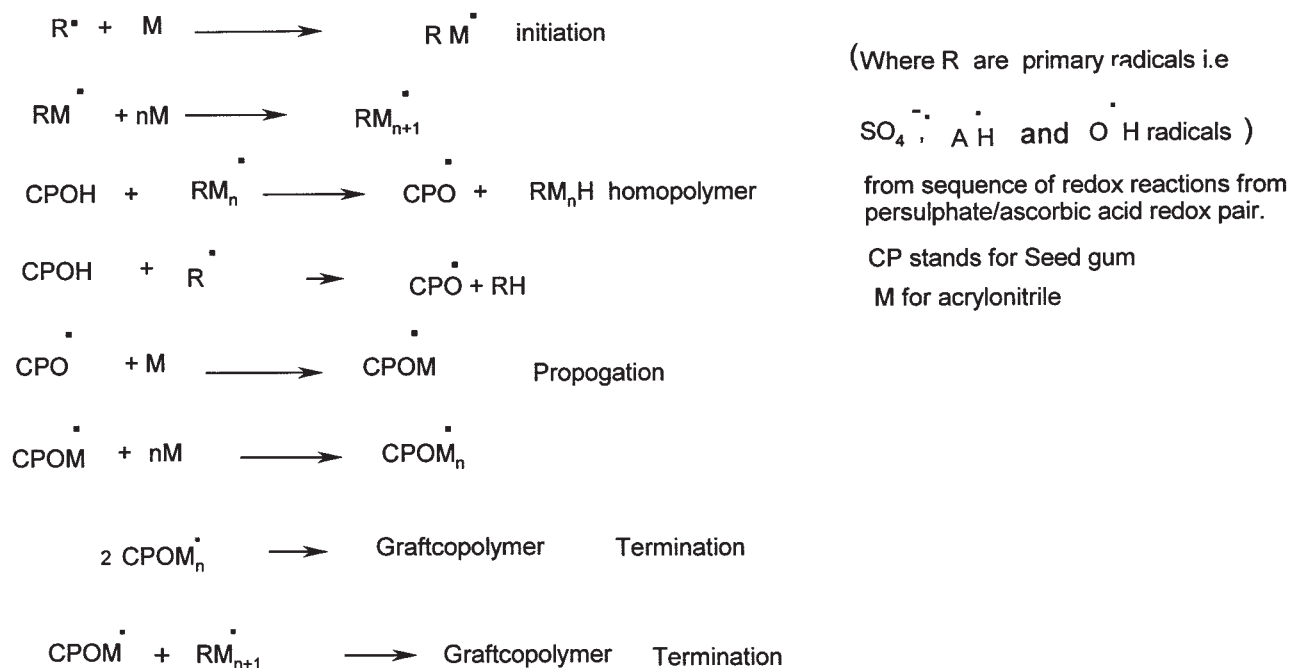
$$\% \text{ Grafting (\%G)} = \frac{W_1 - W_0}{W_0} \times 100 \quad (1)$$

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

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

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Scheme 1 Graftcopolymerization initiated by the primary radicals given by the redox initiator.

Isolation¹⁹ of the seed gum

Seeds (1 kg) of the CP were mechanically ground and sieved with the 100–150 mesh pore size sieves and exhaustively extracted with petroleum ether (60–80°C) in a Soxhlet unit, followed by refluxing with EtOH to remove the coloring matter, and then suspended in 1% aqueous AcOH overnight, mechanically stirred, and filtered. The filtrate (mucilage) of 1% solution was precipitated with 95% EtOH. Dissolution and reprecipitation of the seed gum were repeated six times to get pure seed gum. The crude gum was collected, washed with ethanol, and dried.

Purification

Seed gum was purified¹⁹ 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 1M acetic acid and stirred for 8 h, centrifuged and precipitated with 95% ethanol, and subsequently washed with 70, 80, 90, and 95% ethanol.

Complete hydrolysis and quantification¹⁹ of constituent monosaccharides

The pure seed gum was hydrolyzed with 1M trifluoroacetic acid (4 h, at 100°C). 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 preparation of derivatives: D-galactose phenyl hydrazone, mp 154°C; and D-mannose phenyl hydrazone, mp 198°C.

The ratio of the monosaccharides was determined by GLC.²⁰ The complete hydrolysate of the seed gum was evaporated, the residue was reduced with sodium borohydride, and the product acetylated with Py/Ac₂O (1 : 1 v/v, 1 h at 100°C). The resulting alditol acetates were analyzed by GLC. The ratio of D-galactose to D-mannose was found to be 1.01 : 1.50.

Graft copolymerization

A calculated amount of the CP seed gum was dissolved in minimum required amount of distilled water in a 150 mL flask. To this solution, calculated amount of the AN and AA were added and the total volume was made up to 25 mL. The flask was ther-

TABLE I
Maximum %G and %E Achieved, Gal : Man Ratio, and Viscosity for CP Gum and Guar Gum

S. no.	Gum	Ratio Gal : Man	Maximum %G	Maximum %E	Viscosity 1% solution
1.	Guar gum	1 : 2	177 ¹⁰	51.30 ¹⁰	1340
2.	<i>Cassia pudibunda</i>	1.1.5	294	85.30	82.8

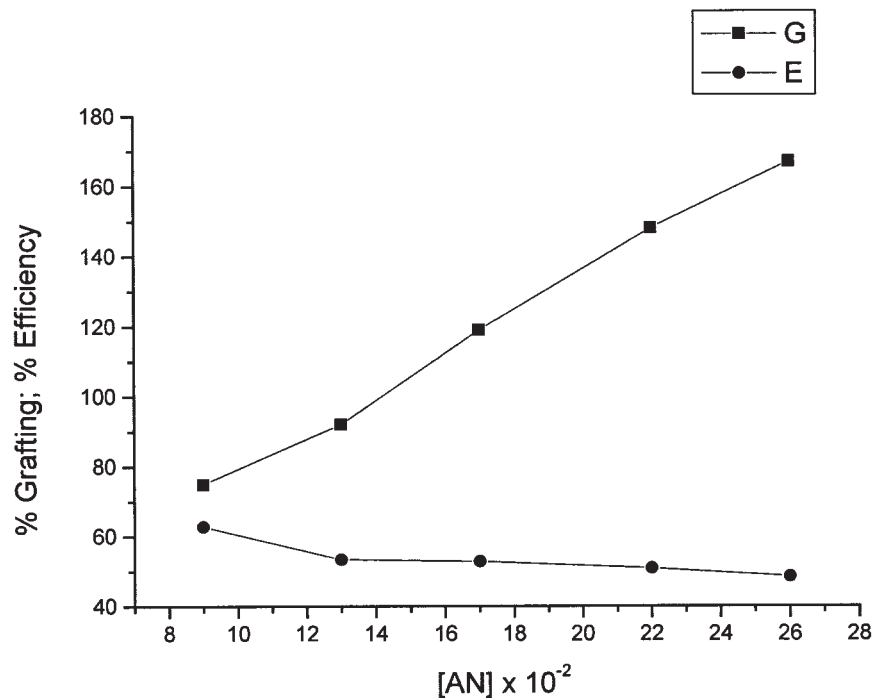


Figure 1 Effect of AN concentration. $[K_2S_2O_8] = 1.0 \times 10^{-2}M$; $[AA] = 2.3 \times 10^{-2}M$; $[CP \text{ gum}] = 4 \text{ g/L}$; and $\text{temp} = 5^\circ\text{C}$.

mostated at $(35 \pm 0.2)^\circ\text{C}$. After 30 min, a definite amount of persulphate was added and this was taken as zero time. Grafting was allowed for 1 h and gum-g-polyacrylonitrile (CP-g-PAN) gum was separated from poly(acrylonitrile) (PAN) by pouring the reaction mixture into large quantity of DMF.¹⁶

Hydrolysis in aqueous alkali

Samples of the grafted CP gum were hydrolyzed¹⁶ in aqueous alkali. Two gram of grafted samples (on dry basis) was dispersed in 1% NaOH at 100°C for 1.5 h. After hydrolysis, the samples were precipitated in 600

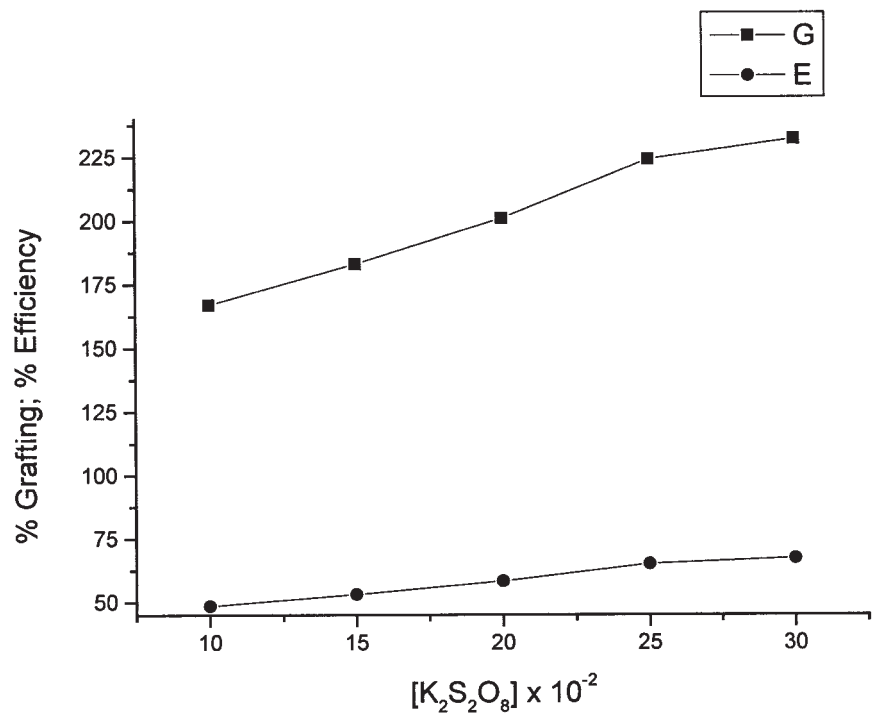


Figure 2 Effect of $K_2S_2O_8$ concentration. $[AN]=26 \times 10^{-2}M$; $[AA] = 2.3 \times 10^{-2}M$; $[CP \text{ gum}] = 4 \text{ g/L}$; and $\text{temp} = 35^\circ\text{C}$.

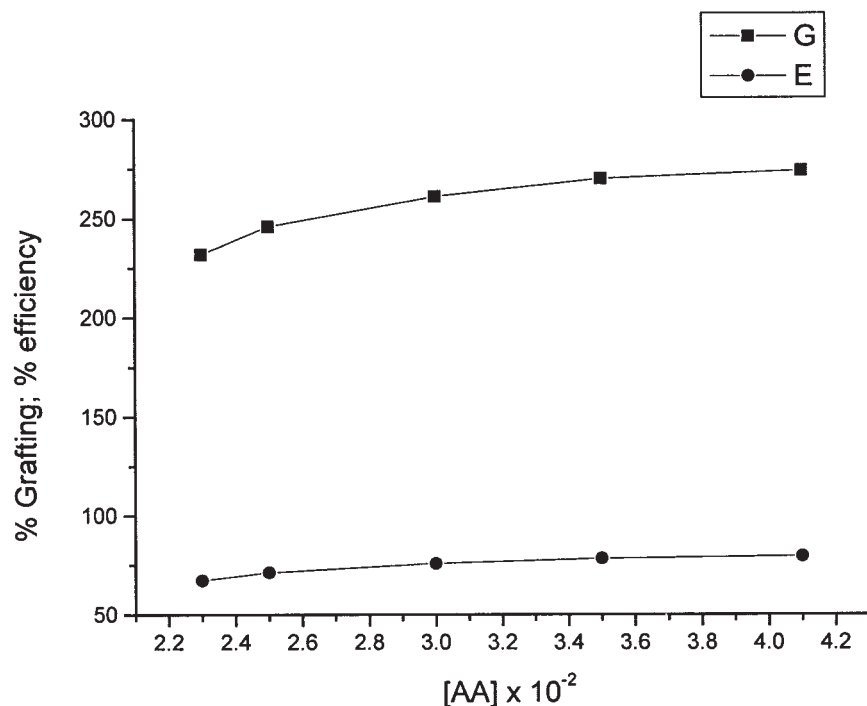


Figure 3 Effect of AA concentration. $[AN] = 26 \times 10^{-2}M$; $[K_2S_2O_8] = 3.0 \times 10^{-2}$; $[CP \text{ gum}] = 4 \text{ g/L}$; and $\text{temp} = 35^\circ\text{C}$.

mL methanol, washed with methanol and ethanol, dried, and weighed.

Water retention of the hydrolyzed samples

Alkali-hydrolyzed sample (0.5 g; on dry basis) was swollen¹⁶ in 100 mL distilled water separately for 10

min. The suspension was poured into a sintered glass filter (porosity 1) at 700 mmHg pressure in each case. The volume of the filtrate was measured and water retention calculated as gram of water per gram of dry material. The measurement was repeated after drying the hydrolyzed samples in an oven at 60°C .

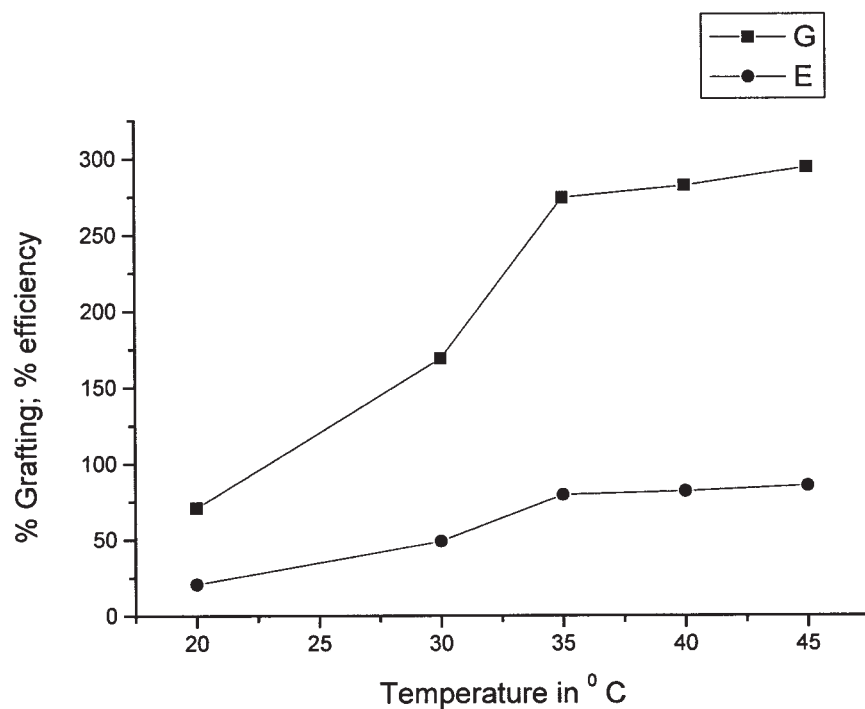


Figure 4 Effect of temperature. $[AN]=26 \times 10^{-2}M$; $[K_2S_2O_8] =3.0 \times 10^{-2}M$; $[AA] =4.1 \times 10^{-2}M$; and $[CP \text{ gum}]=4 \text{ g/L}$.

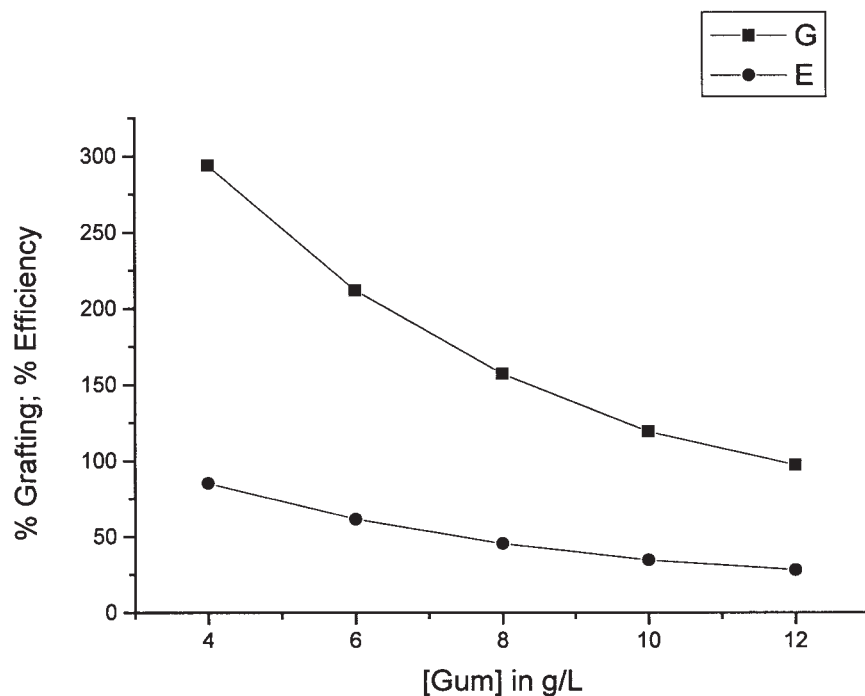


Figure 5 Effect of CP gum concentration. $[AN] = 26 \times 10^{-2}M$; $[K_2S_2O_8] = 3.0 \times 10^{-2}M$; $[AA] = 4.1 \times 10^{-2}M$; and temp = 45°C.

RESULTS AND DISCUSSIONS

Complete acid hydrolysis has shown CP seed gum to be a galactomannan-like guar gum, however, the ratio of the monosaccharides as determined by GLC was found to be 1.01 : 1.50 in comparison to 1 : 2 in the guar

gum. The viscosity of 1% CP gum solution was observed to be quite less than guar gum, indicating its lesser molecular mass. Since CP seed galactomannan is different from guar gum in its finer structure, different grafting behavior and in turn different proper-

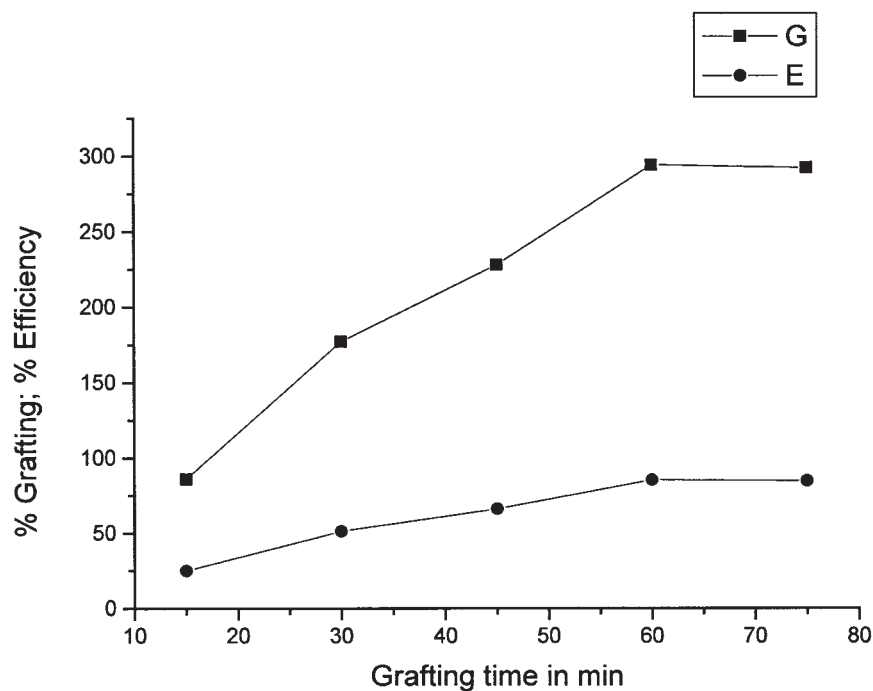


Figure 6 Effect of guar gum concentration. $[AN] = 26 \times 10^{-2}M$; $[K_2S_2O_8] = 3.0 \times 10^{-2}M$; $[AA] = 4.1 \times 10^{-2}M$; and temp = 45°C.

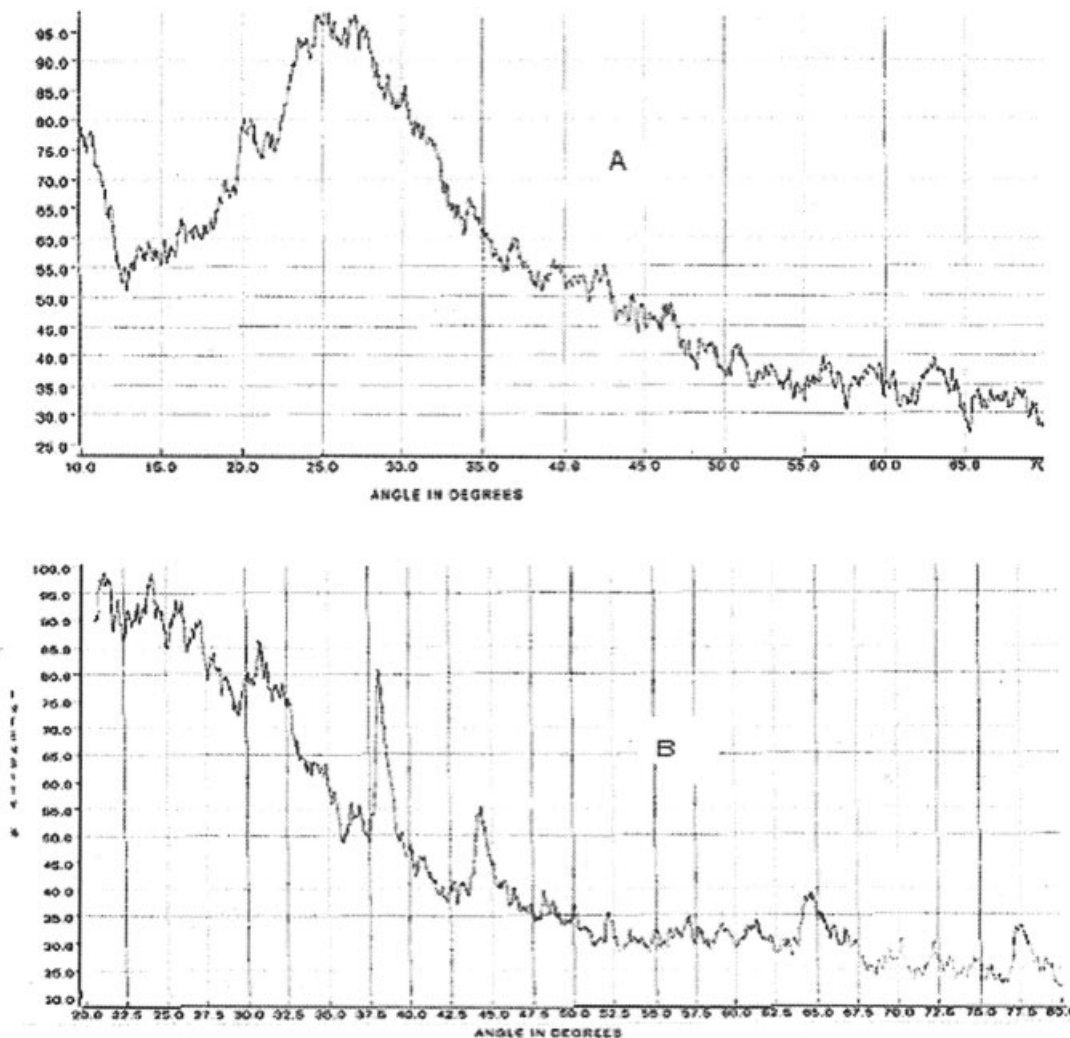


Figure 7 (A) XRD of the pure gum and (B) XRD of CP-g-PAN.

ties are expected for graft copolymer from CP compared with those of gaur gum.

Mechanism of grafting

Mehrotra and Mushran²¹ studied the kinetics of the redox system containing AA and peroxydisulphate and a mechanism involving $\text{SO}_4^{\cdot-}$, 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 AN copolymerization with seed gums. Reaction between persulphate and AA involves a chain mechanism²³ due to the formation of sulfate ion radicals, which are well-known ion chain carriers.

$\text{SO}_4^{\cdot-}$, OH^{\cdot} , and AH^{\cdot} (ascorbate radical), the primary radicals, generated by persulphate/AA redox reactions are expressed as R in the Scheme 1. They initiate the vinyl polymerization, as vinyl polymerization is reported to be faster than the H abstraction from the

seed gum backbone. The macroradical (CPO^{\cdot}) may be generated by the abstraction of H, which may add on to the vinyl monomer (M) generating new radical CPOM^{\cdot} 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 condition for grafting of AN on to the CP gum, the concentration of monomer, potassium persulphate, AA, CP gum, reaction temperature, and reaction time were varied keeping total volume of the reaction mixture fixed at 25 mL. It was observed that $\text{K}_2\text{S}_2\text{O}_8/\text{AA}$ redox system can be efficiently used to graft AN on to CP gum where maximum %G and %E (Table I) could be achieved 294 and 85.34%, respectively.

Effect of monomer concentration

The increase in the concentration of monomer from 9×10^{-2} to $26 \times 10^{-2} \text{M}$ results in the increase of %G

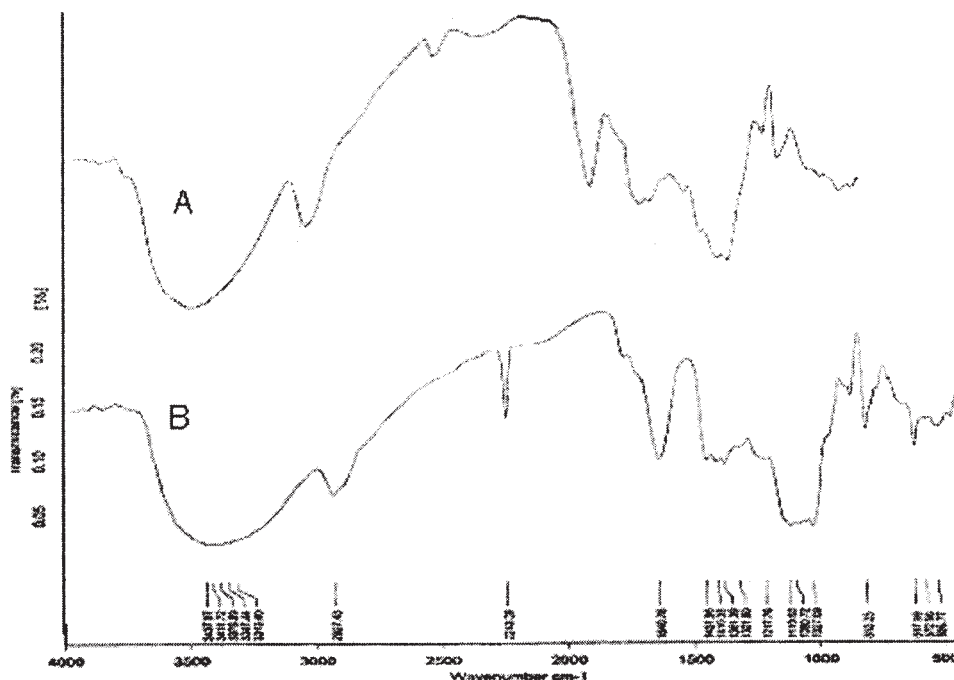


Figure 8 (A) IR spectra CP gum; (B) IR of CP-g-PAN.

under the fixed concentration of AA ($2.3 \times 10^{-2}M$), $K_2S_2O_8$ ($1 \times 10^{-2}M$), and CP gum (4 g/L) at (35 ± 0.2)°C (Fig. 1). The increase in %G may be due to the formation of more M_n while generating more grafting sites and availability of more monomer for grafting. Increasing concentration beyond $9 \times 10^{-2}M$, the %E decreased slightly, and this may be because of further increase in the monomer free radicals may promote homopolymerization that competes the graftcopolymerization.

Effect of persulphate concentration

%G and %E increased with increase in initiator concentration and reached a maximum value at $3.0 \times 10^{-2}M$ persulphate at fixed concentration of $26 \times 10^{-2}M$ AN, $2.3 \times 10^{-2}M$ AA, and 4 g/L gum at (35 ± 0.2)°C (Fig. 2). The observed increase in %G and %E with increase the persulphate concentration ranging from 1×10^{-2} to $3.0 \times 10^{-2}M$ 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 backbone. An increase in %E with the persulphate concentration increase may be because of the consumption of the growing monomer free radicals at activated sites on the backbone for grafting, reducing the chances for the homopolymerization.

Effect of AA concentration

The effect of AA was studied in the range 2.0×10^{-2} – $4.1 \times 10^{-2}M$ at fixed concentration of AN (26

$\times 10^{-2}M$), potassium persulphate ($3.0 \times 10^{-2}M$), and CP gum (4 g/L) at (35 ± 0.2)°C (Fig. 3). It was observed that both %G and %E increases with the increase in the concentration of AA, which may be due to the generation of more primary free radicals that can generate more grafting sites retarding the homopolymerization.

Effect of temperature

The grafting reaction was carried out at different temperature (20–45°C) keeping other variables constant [$K_2S_2O_8$] $3.0 \times 10^{-2}M$; [AA] $4.1 \times 10^{-2}M$; [AN] $26 \times 10^{-2}M$; and [Gum] 4 g/L (Fig. 4). Maximum %G was obtained at 45°C. The observed increase in %G and %E 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.

Effect of gum concentration

The effect of gum concentration was studied in the range of 4–12 g/L with the constant [$K_2S_2O_8$] $3.0 \times 10^{-2}M$, [AA] $4.1 \times 10^{-2}M$, and [AN] $26 \times 10^{-2}M$ at $35^\circ C \pm 0.2^\circ C$ (Fig. 5). It was found that both %G and %E are maximum at 4 g/L gum concentration, thereafter the %G and %E decreases that may attributed to the increase in the viscosity of the reaction medium causing hindrance of the normal reaction.

Effect of reaction time

The grafting reaction was carried out at different time intervals (15–75 min) keeping other variables constant

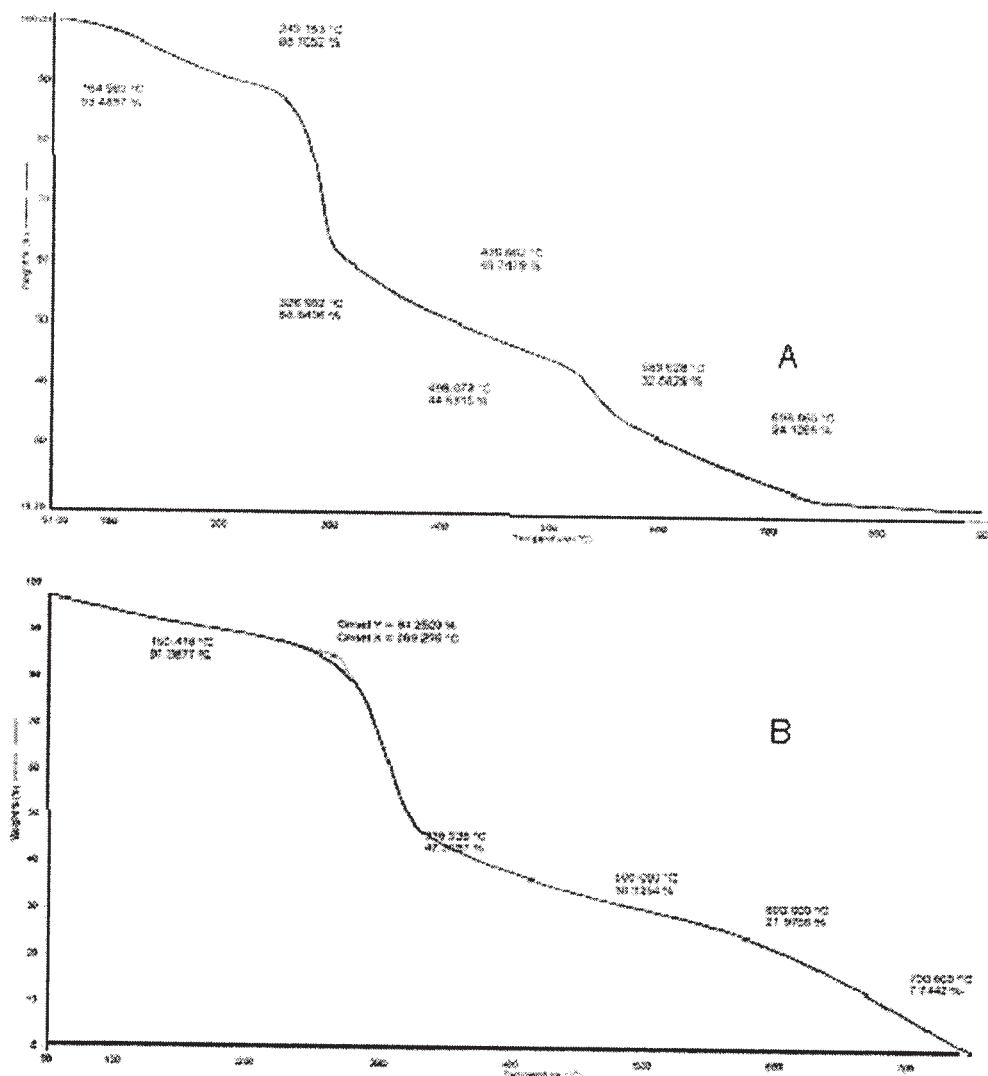


Figure 9 (A) TGA spectra CP gum; (B) TGA spectra of CP-g-PAN.

$[K_2S_2O_8]$ $3.0 \times 10^{-2}M$; $[AA]$ $4.1 \times 10^{-2}M$; $[AN]$ $25 \times 10^{-2}M$; and $[CP\ Gum]$ 4 g/L at 45°C (Fig. 6). 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 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 for guar gum was 294 and 85.3% with $[K_2S_2O_8]$ $3.0 \times 10^{-2}M$; $[AA]$ $4.1 \times 10^{-2}M$; and $[AN]$ $26 \times 10^{-2}M$; $[CP\ Gum]$ 4 g/L at 45°C.

Characterization of the grafted gum

XRD of CP gum is compared with the grafted CP gum (Fig. 7). XRD spectra of the grafted CP gum showed additional sharp peaks in the region 2θ 20–27° and

37–45° corresponding to the crystallinity of grafted PAN on CP gum backbone.

IR spectrum of pure CP has a broad strong band at 3410 cm^{-1} , a band at 2900 cm^{-1} indicating C—H linkages, while IR spectra of grafted CP gum have strong absorption peaks at 2244 cm^{-1} for —CN stretching, and CH_2 deformation vibration at 1451 cm^{-1} (Fig. 8). Physical blend of CP gum and PAN after selective removal of PAN with dimethylformamide (DMF) showed no absorption in —CN stretching and — CH_2 bending region. This substantiates the formation of the graft copolymer.

The TGA of the grafted gums (Fig. 9) shows that decomposition of the CP gum onsets at 243.1°C and shows 6.6% weight loss at 164.5°C, which may be attributed to adhered water molecules, thereafter the gum decompose slowly and up to 698°C a weight loss of 95.9% occurs. TGA of CP-g-PAN also shows loss of adhered water at 150°C but thereafter

TABLE II
Viscosity, Water Retention, and Saline Retention of CP Gum, CP-g-PAN, and Alkali-Hydrolyzed CP-g-PAN

S. no.	Gum	Water retention in 10 min	Saline retention in 10 min	Viscosity of 1% solution (centipoises)
1.	CP gum	16.20	11.40	82.8
2.	CP-g-PAN	7.70	5.20	Water insoluble
3.	Alkali-hydrolyzed CP-g-PAN	47.03	30.150	114.7

decomposition onsets at 269°C, showing grafted gum to be more thermally stable than the parent gum.

Water and saline retention

Water and saline retention of the grafted CP gum (sample with maximum %G) after hydrolysis with alkali was shown to be 47.02 and 30.150 g/g, respectively, after 10 min soaking. On hydrolysis with alkali, the nitrile groups at CP-g-PAN get hydrolyzed in to —COOH and CONH₂ groups, which offer additional binding sites thus increasing water and saline retention when compared with CP-g-PAN. The hydroxy groups at the parent CP gum are water binding sites, and after grafting, some of them are grafted and thereby reducing the water and saline retention in CP-g-PAN. Water and saline retention of parent gum, grafted gum, and alkali-hydrolyzed grafted gum have been compared in Table II.

The viscosity of the alkali-hydrolyzed gum on leaving at room temperature increased initially (Table III), this may be due to the some possible intramolecular interaction of the —COOH groups at the grafted chains, which acquire stability after some time.

CONCLUSIONS

CP seed gum can be very efficiently grafted with persulphate/AA redox system, and the gum after grafting develops properties that can be exploited in-

dustrially. Grafted gum after hydrolysis with alkali may find use as water sorbents and its solutions may furnish stable gum solutions of medium to low viscosity.

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References

- Kirtikar, K. R.; Basu, B. D. In *Indian Medicinal Plants*, 2nd ed.; Blatter, E., Ed.; Bishen Singh Mahendra Palsingh: Dehradun, 1932; Vol. 3, p 1715.
- Lindlet, J. In *Flora Medica: A Botanical Account*; Ajay Publishing Works: Delhi, India, 1981; p 260 (Indian reprint).
- Mark, H. F.; Bikales, N. M.; Overberger, C.; Menges, G. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Wiley: New York, 1987; Vol. 7, p 597.
- Mark, H. F.; Gaylord, N. G.; Bikales, N. M. In *Encyclopedia of Polymer Science and Technology*; Wiley Interscience: New York, 1967; Vol. 6, p 275.
- Bajpai, U. D. N.; Rai, S. J *Appl Polym Sci* 1988, 35, 1169.
- Hinkelar, D. *Macromolecules* 1991, 24, 2160.
- Bajpai, U. D. N.; Jain, A.; Rai, S. J *Appl Polym Sci* 1990, 39, 2187.
- Bajpai, U. D. N.; Mishra, V.; Rai, S. J *Appl Polym Sci* 1993, 47, 717.
- Chowdhury, P.; Samui, S.; Kundu, T.; Nandi, M. M. *J Appl Polym Sci* 2001, 82, 3520.
- Singh, V.; Tiwari, A.; Tripathi, D. N.; Sanghi, R. *J Appl Polym Sci* 2004, 92, 1569.
- Singh, V.; Tiwari, A.; Tripathi, D. N.; Sanghi, R. *Carbohydr Polym* 2004, 58, 1.
- Singh, V.; Srivastava, A.; Srivastava V.; Pandey, M.; *Nat Acad Sci Lett* 2002, 25, 294.
- Gupta, R.; Khare, N.; Singh, V.; Gupta, P. C. *Carbohydr Res* 1987, 159, 336.
- Kumar, P.; Singh, V.; Mishra, U. C.; Gupta, P. C. *Carbohydr Res* 1990, 198, 384.
- Mishra, U. C.; Singh, V.; Shukla, R.; Dixit, A. K.; Gupta, P. C. *Int J Pharmacognosy* 1991, 29, 14.
- Singh V.; Tiwari, A.; Tripathi, D. N.; Sanghi, R. *Biomacromolecules* 2005, 6, 453.
- Sharma, B. J; Kumar, V.; Soni, P.L. *Trends Carbohydr Chem* 1999, 5, 5.
- Wunderlich, T.; Stelter, M. T.; Tripathy, B. R.; Nayak, G.; Brenn, A.; Yarin, I.; Singh R. P.; Brunn, P.O.; Durst, F. *J Appl Polm Sci* 2000, 77, 3200.
- Singh, V.; Srivastava, V.; Pandey, M.; Sethi, R.; Sanghi, R. *Carbohydr Polym* 2003, 51, 357.
- Kapoor, V. P.; Chanzy, H.; Travel, F. R.; *Carbohydr Polym* 1995, 27, 229.
- Mehrotra, U. S.; Mushran, S. P. *J Ind Chem Soc* 1970, 47, 41.
- Mushran, S. P.; Agrawala, M. C. *J Sci Ind Res* 1977, 36, 274.
- Singh, V.; Tiwari, A.; Sanghi, R. J.; *Appl Polym Sci* 2005, 98, 1652.

TABLE III
Viscosity of 0.25% Solution of Alkali-Hydrolyzed CP-g-PAN with Time on Standing at Room Temperature

S. no	Time (h)	Viscosity of 0.25% CP gum (centipoises)
1.	00	12.51
2.	24	18.48
3.	48	22.92
4.	72	25.35
5.	96	27.05
6.	120	28.32
7.	148	28.32
8.	172	28.32
9.	196	28.32
10.	220	28.32
11.	244	28.32
12.	384	28.32