

Water-Superabsorbent Polymers through Gamma Radiation-Induced Graft-Copolymerization of Acrylonitrile on Guar gum

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SYNOPSIS

Superabsorbent polymers based on guar gum have been prepared through a graft-copolymerization reaction using acrylonitrile as the monomer by a gamma ray-induced irradiation technique. Various grafting parameters have been studied. The grafted products have been characterized using infrared spectroscopy, thermogravimetric, and differential thermal analysis. The thermograms reveal the superior thermal stability of the grafted product over the control at all stages of its degradative cycle. The maximum absorbency obtained of the superabsorbent product was around 300 g/g.

INTRODUCTION

The technique of polymer grafting is one of the methods used for the preparation of superabsorbent polymers. Much work has been carried out on natural polysaccharides such as starch¹⁻⁴ and cellulose⁵⁻⁷ for the preparation of superabsorbent products using the above technique. Guar gum is one such naturally occurring polysaccharide. It is a branched polymer with β -D-mannopyranosyl units linked (1 \rightarrow 4) with single-membered α -D-galactopyranosyl units occurring as side branches.⁸ This polymer finds extensive applications in various industries like textiles, paper, food, oil well drilling, etc., either as such or in the form of various derivatives such as hydroxyethyl, hydroxypropyl, and carboxymethyl. Many modification treatments have been attempted on this material for the preparation of superabsorbents. These modifications, in general, involve cross-linking agents or incorporating a saltlike zinc borate.⁹ Derivatives¹⁰ of guar gum have also been used to prepare superabsorbents. Deshmukh and Singh¹¹ studied some rheological properties and biodegradability of guar gum grafted with vinyl monomers.

Menaria et al.¹² also reported some work on the grafting of guar gum. Both the above investigations made use of the well-known ceric ion method of initiation for grafting. In the present work, an attempt is made to carry out graft copolymerization of acrylonitrile on guar gum using gamma ray radiation as the initiator employing simultaneous irradiation techniques and to study the various properties of the grafted as well as the absorbent material prepared out of the grafted gum.

EXPERIMENTAL

Guar gum powder of edible grade (M/s Hazrat & Co.) were used for modification treatments. To determine the effect of gamma ray radiation on unmodified raw guar gum, aqueous dispersions of 1% slurry of the material was prepared in a blender at room temperature ($30 \pm 1^\circ\text{C}$). The slurry was allowed to swell for 1 h. These were irradiated to various dose levels at ambient temperature from a cobalt-60 source at a dose rate of 0.2 Mrads/h. The cobalt-60 source was supplied by Bhabha Atomic Research Centre, Bombay. During irradiation, no attempt was made to control the rise in temperature. The viscosities of the control and irradiated dispersions were measured in a Brookefield viscometer (Model RV).

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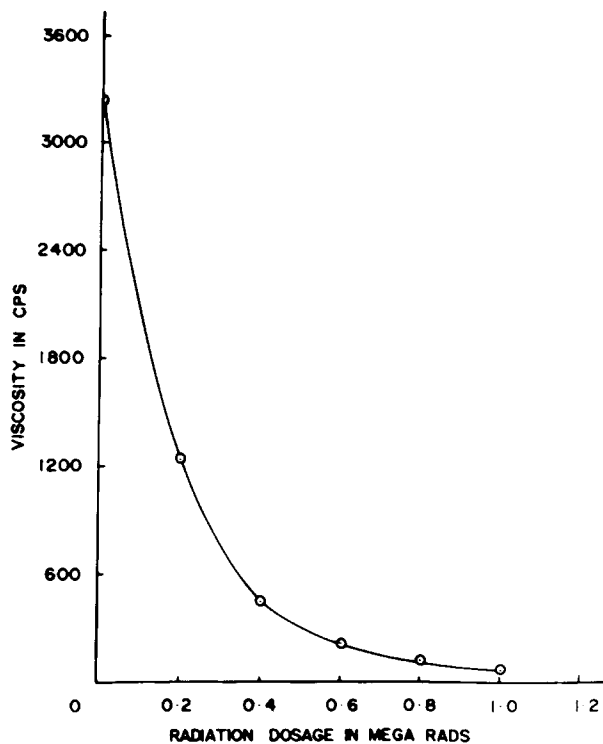


Figure 1 Effect of gamma radiation on 1% aqueous dispersion of guar gum.

Preparation of the Grafted Products

Ten grams (dry weight) of guar gum was mixed well with 20 mL of distilled water and 10 g freshly distilled acrylonitrile (AN) (S. D. Fine-Chemicals Ltd.) in a blender. The samples were irradiated to five different dosages of radiation under the conditions

described above. After irradiation, the unpurified grafted samples were washed with water to remove the unreacted AN. To the water-washed product, 400 mL methanol was added and shredded in a blender. The product was filtered and dried at room temperature ($30 \pm 1^\circ\text{C}$). The unreacted portion of the gum was removed by extracting with water at 90°C for 2 h. The crude product was extracted with 500 mL dimethylformamide (DMF) for 24 h at room temperature. This was filtered and washed with fresh DMF, followed by water and methanol. The purified product was dried at room temperature. Grafting was confirmed by IR analysis, and percentage grafting was calculated by an increase in weight as well as by nitrogen estimation.

Saponification

A mixture of 10.00 g (dry weight) of purified grafted product and 90 mL of 0.7*N* potassium hydroxide was taken in a loosely stoppered Erlenmeyer flask and heated in an oven at 100°C for 2.5 h. After the reaction, the mixture was cooled to room temperature and the pH of the mass was adjusted to 8.0 with glacial acetic acid. The mixture was then blended with 450 mL methanol. The solid was separated by filtration, washed twice with methanol, and allowed to air-dry. Infrared spectra showed complete nitrile saponification.

Molecular Weight of Grafted Side Chain

The grafted side chain was separated through acid hydrolysis employing 1*N* HCl as described by Gugliemelli et al.¹ The hydrolysis was carried out for 4

Table I Grafting Parameters at Different Radiation Doses

Sample No.	Dosage (Mrad)	Wt. of Crude after Water and Alcohol Wash ^a (g)	Wt. after DMF Extraction ^a (g)	Grafting ^b (%)	PAN ^c (%)	Molecular Weight of PAN Side Chain ($\times 10^5$)	Frequency of Grafting (AGU/graft)
1	0.1	13.5	13.0	37.1	—	—	—
2	0.2	—	—	41.3	39.8	3.675	3431
3	0.3	15.4	14.6	45.4	43.9	3.877	3058
4	0.4	16.2	15.5	47.7	48.7	3.962	2576
5	0.5	15.6	15.3	43.9	45.7	3.385	2483
6	0.6	17.6	16.2	45.0	46.2	3.305	2376
7	0.7	15.8	15.3	48.4	44.8	2.821	2146
8	0.8	17.5	16.3	52.2	46.1	2.821	2036
9	0.9	18.9	16.8	46.9	46.8	2.821	1980

^a Samples were air-dried (g (%) moisture).

^b By nitrogen estimation.

^c By acid hydrolysis.

Table II Properties of Final Product

Sample No.	Dosage (Mrad)	Viscosity ^a (Brookefield) (cps)	Water Absorbency (g/g)
1	0.2	2300	262
2	0.4	2300	279
3	0.6	3450	295
4	0.8	3750	274
5	0.9	2000	239

^a Spindle no. 4 RPM 20 at room temperature.

h instead of 2 h for the complete dissolution of PAN in DMF. The number-average molecular weight of polyacrylonitrile (PAN) was calculated from the Mark-Houwink equation using Onyon's constants.¹³

Viscosity of the Saponified Product

Viscosity of 1% aqueous slurry of the saponified product was determined by a Brookefield viscometer (Model RV).

Water Absorbency

The method adopted by Fanta et al.¹⁴ was used for absorbency tests.

Infrared Analysis

The spectra were recorded in the KBr phase by using a Perkin-Elmer Model 457 I.R. spectrophotometer employing the KBr pellet technique of O'Connor et al.¹⁵

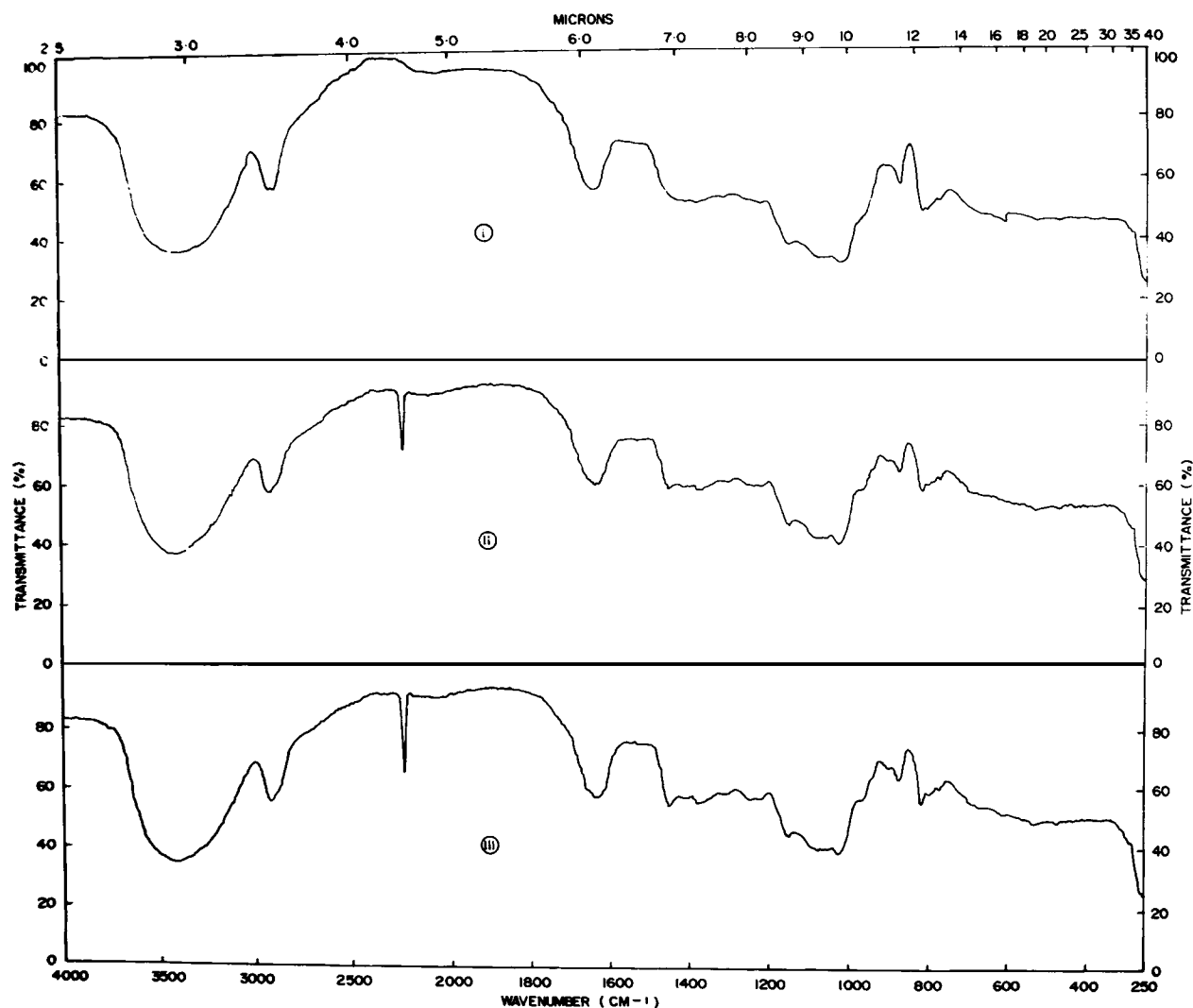


Figure 2 Infrared spectra of PAN grafted guar gum: (1) unmodified guar gum; (2) percent graft, 37.1; (3) percent graft, 46.9.

Table III Tentative Assignment of IR Absorption Bands of Guargum

Wave Length (Micron)	Wavenumber (cm^{-1})	Assignment
6.1	1640	Adsorbed H_2O
7.0	1430	CH_2 symmetrical bending
7.25	1380	C—H deformation
8.7	1149	C—O—C antisymmetrical stretching
9.8	1030	C—O skeletal stretching/C—C stretching
10.3	970	Ring symmetrical vibration (pulsation)
11.5	870	C—H deformation

Differential Thermal Analysis (DTA) and Thermogravimetric Analysis (TGA)

The above thermal analysis was carried out using a Mettler thermobalance TAHE.20. The sample size was about 10 mg. The sample was heated in a quartz crucible to 680°C at the rate of $10^\circ\text{C}/\text{m}$. Alumina were used as a reference. The studies were carried out in air for DTA. The primary thermogram was automatically recorded. The percentage weight loss at different temperatures was calculated from the primary thermogram. Initial decomposition temperature (*idt*) and integral procedural decomposition temperature (*ipdt*)¹⁶ were also calculated.

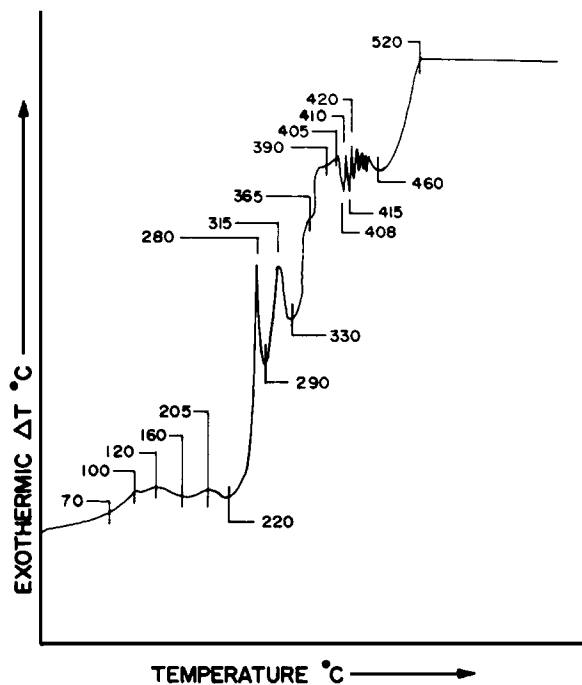
RESULTS AND DISCUSSION

Figure 1 depicts the effect of gamma ray irradiation on the 1% aqueous dispersion of raw guargum. A continuous fall in the viscosity of the dispersion was observed with an increase in the radiation dose.

Table I presents various grafting parameters at different dosages of radiation. There is an increase in the grafting percentage from 37.1% at 0.1 Mrad dosage to 47.7% at 0.4 Mrad. Subsequently, no appreciable increase in grafting percentage is observed up to 0.9 Mrad. The PAN percentage calculated from acid hydrolysis agrees well with the grafting percentage obtained through N% estimation. The number-average molecular weight of the grafted side chain registers a slight increase up to a 0.4 Mrad dose level and then shows a downward trend with further increase of radiation dose. Also, despite the decrease in the number-average molecular weight, the percentage graft almost levels off from 0.5 Mrad onward. This may be due to the increase in the number of grafted side chains having shorter chain lengths. This observation is further confirmed by

the increase in the frequency of grafting with increase in the radiation dose.

Table II depicts the values of absorbency and the viscosity of the aqueous dispersions of the saponified product. The values of the absorbency are fairly constant around 270 g/g for all the dosages. These values are comparable to those reported earlier for starch-based superabsorbents.¹⁴ The viscosity values of the dispersions are contrary to the expectation. There is no improvement in the viscosity values over the raw guargum. This may be due to the degradative effect of gamma irradiation on the polysaccharide backbone. Similar effects for starch have been reported by Taga and Inagaki,¹⁷ Min and Inagaki,¹⁸ and Iyer et al.¹⁹ The degradative effect of radiation

**Figure 3** DTA graph of grafted guargum (45%).

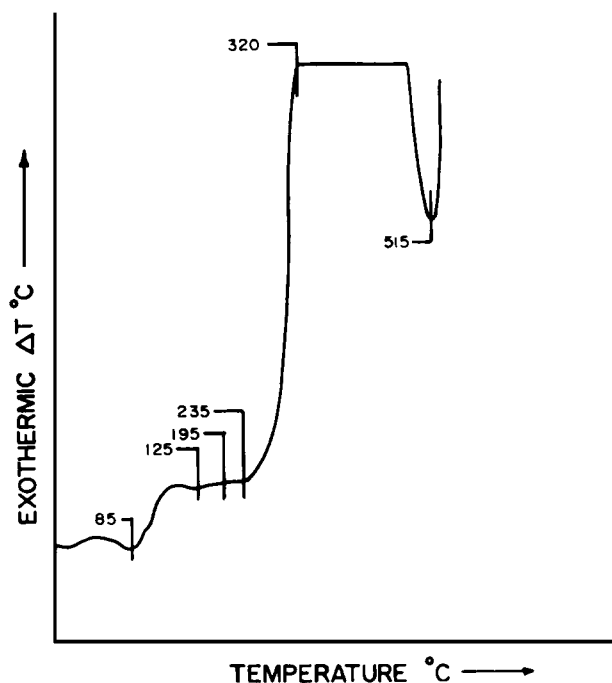


Figure 4 DTA graph of guar gum.

on the aqueous dispersion of raw guar gum (Fig. 1) also confirms the above view.

The infrared absorption spectra of grafted as well as ungrafted guar gum is presented in Figure 2. Based on the general considerations for the assignment of various absorption bands of cellulose and other related polysaccharides^{20,21} and the work on guar gum by Gulrajani and Roy Chaudhury,²² a tentative assignment of IR absorption bands of guar gum in the region of 5–12 μ is presented in the Table III. The spectra of purified grafted guar gum shows the characteristics $C\equiv N$ absorption band at 2240 cm^{-1} . It is also noted that the intensity of the above absorption band increases with increase in the percentage grafting.

The DTA and TGA profiles of raw, unmodified guar gum and the purified grafted products are presented in Figures 3–5. Their decomposition temperatures at various stages are presented in Table IV. In the DTA graph of the control, the endothermic reaction around 85–100°C represents the loss of sorbed moisture. From 135 to 235°C, no well-defined reactions seem to occur, which is in conformity with the TGA profile of the control sample, where very little weight loss is noted in this region. The exothermic reaction observed in the region of 235–320°C is once again supported by the drastic reduction in the sample weight observed in the TG degradative profile in Figure 5.

In contrast to the control, the DTA graph and

TG profile of the grafted product shown in Figures 3 and 5 present a different pattern. In the DTA graph of the grafted sample, the region up to 100°C depicts a minor endothermic reaction due to the loss of sorbed moisture. The absence of a prominent endothermic peak in this region as observed in the control sample may probably be due to the lower initial moisture content of the sample. The region between 100°C to around 200°C is marked by low activity with two minor exothermic peaks around 120°C and 205°C. The TG profile of the grafted sample is in conformity with the above observation. The region around 220°C to 280°C marks the occurrence of an exothermic reaction that is showing up in the TG profile in Figure 5. The region between 300 and 520°C is a high reactivity region on the whole and markedly different from that of the control. The TG degradative profile once again is in agreement with the above observation.

The exothermic process observed in this region probably involves the formation of new products from the fragmentation products of the polysaccharide and the PAN side-chain grafts. The thermograms and the degradative pattern shown in Table III bring out the superior thermal stability of the purified grafted product at all stages of the degradative cycle. The above observation is further confirmed by the higher *ipdt* values of the grafted sample.

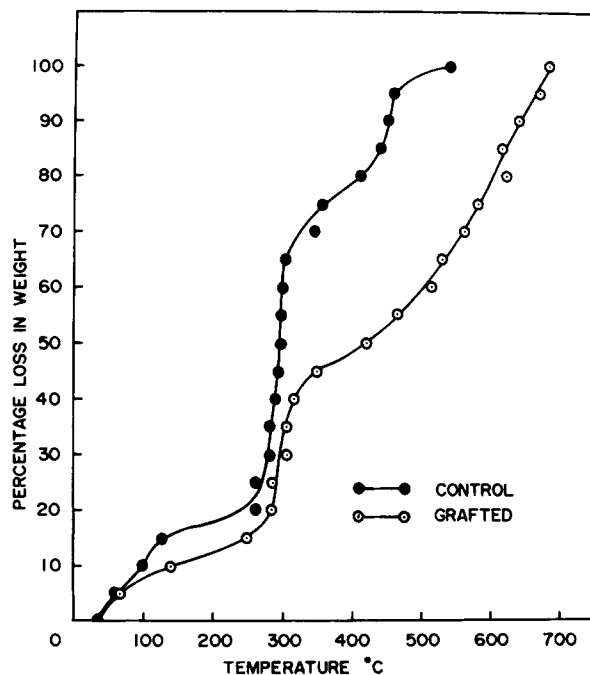


Figure 5 TGA graph: (a) raw guar gum; (b) grafted guar gum (45%).

Table IV TGA Data Showing Loss in Weight of Samples at Different Temperatures

Temperature (°C)	Percentage Weight Loss	
	Control	Grafted
50	2.5	2.0
100	10.5	7.5
150	14.0	10.5
200	16.5	12.5
250	19.0	15.5
300	63.5	38.5
350	72.5	45.0
400	80.0	49.0
450	90.0	53.5
500	—	60.0
550	—	69.0
600	—	78.0
650	—	88.5

ipdt values: control, 345.3; grafted, 452.7.

The present study indicates the possibility of carrying out graft copolymerization reactions onto this plant-derived polysaccharide for the preparation of superabsorbents.

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