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Microwave assisted synthesis of Guar-g-polyacrylamide

Vandana Singh[a,*], Ashutosh Tiwari[a], Devendra Narayan Tripathi[a], Rashmi Sanghi[b]

[a]*Department of Chemistry, University of Allahabad, A202, Govindpur Colony, Allahabad-211002, India*
[b]*302 Southern Laboratories, Facility fsor Ecological and Analytical Testing, Indian Institute of Technology, Kanpur-208016, India*

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Abstract

Microwave (MW) assisted synthesis of guar-g-polyacrylamide (G-g-PAA), a co-polymer of wide applications is being reported in the present communication. Graft co-polymerization of the guar gum (GG) with acrylamide (AA) under the influence of MW in absence of any radical initiators and catalyst resulted in grafting yields comparable to redox (potassium persulphate/Ascorbic acid) initiated conventional heating graft co-polymerization in very short reaction times. The grafting efficiency up to 20% was further increased when initiators and catalyst were used with MW heating. The effect of MW power and exposure time on the grafting yields, both in presence and in absence of redox initiator and catalyst were studied. Maximum grafting efficiency achieved under MW was 66.66% in 0.22 min in comparison to 49.12% in 90 min by the conventional method. A representative MW grafted copolymer was characterized using IR, ^{1}H NMR, XRD and TGA.

Keywords: Microwave irradiation; Graft co-polymerization; Acrylamide; Guar gum; Potassium persulphate/ascorbic acid

1. Introduction

Guar gum is an edible carbohydrate polymer (Whistler, 1969) found in the seeds of *Cyanaposis tetragonolbus* It is non-ionic, branched chain polymer, consisting of straight chain of mannose units joined by β-D (1 → 4) linkages having α-D-galactopyranose units attached to this linear chain by (1 → 6) linkages. The gum forms viscous colloidal dispersions when hydrated in cold water (Bajpai, Jain & Bajpai, 1990a,b). It is as a viscosity builder and water binder in many industries like mining, textile, explosive, paper and petroleum etc. Although advantageous, this viscosity is difficult to control because of its quick biodegradation (Deshmukh & Singh, 1987; Deshmukh, Chaturvedi, & Singh, 1985) and this limits its value for some applications.

Modification of GG by grafting of water-soluble vinyl monomers, results in the retention of desirable properties and incorporation of favorable properties. Such grafted GG is used in the preparation of flocculants (Sharma, Kumar, & Soni, 1999) for industrial requirements and as a biodegradable drag reducing agent. (Wunderlich et al., 2000). Crosslinked G-g-PAA based crosslinked anionic microgels as a pH sensitive drug delivery system have been recently reported. (Soppimath, Kulkarni, & Aminabhavi, 2001). Grafting of wool, nylon and fibers through redox initiation has been investigated in detail but grafting of water-soluble vinyl monomers on a water-soluble natural polymer is quite rare (Bajpai & Jain, 1993; Taunk & Behari, 2000). Concurrent homopolymer formation is the main constraint in graft co-polymerization leading to low grafting yields. MW irradiation (Galema, 1997) to induce very rapid heating, becoming a standard technique in various fields of chemistry. Grafting of butylacrylate (Xiao, Zheng, Yan-Bing, Zefang, & Changyi, 2000), acrylic acid (Yanbin, Xiaoxia, Zefang, & Changyi, 1999) and acrylonitrile (Huang & Chen, 1999) onto starch, grafting of acrylamide on to LLDPE (low density polyethylene) films (Gupta, Anjum, & Gupta, 2000) and grafting of butyl methacrylate on to the wool fibers (Gabriel, Gabriel, Grant, Halstead, & Mingos, 1998) have involved the use of MW irradiation. Polymerization of methylmethacrylate with low concentration of initiating system under MW irradiation has been also reported very recently (Zhenping, Xiulin, Mingchen, & Lifen, 2003). Nevertheless for the first time it has been used in grafting of PAA on to GG. As MW are reported a source of free radicals we were prompted to study if grafting is possible without using any initiator or catalyst under MW

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[*] Corresponding author. Tel.: +91-5322461518; fax: +91-5322545021.
E-mail address: vanchem@idiatimes.com (V. Singh).

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irradiation and surprisingly we could successfully achieve grafting of PAA onto the GG under MW irradiation without the use of any radical initiators or catalyst. Polyacrylonitrile was also successfully grafted (Singh, Srivastava, Pandey, Sethi, & Sanghi, 2003) on to guar gum under microwave irradiation with out any catalyst and/or radical initiator.

2. Experimental

A Kenstar (Model No MOW 9811, 1200 W) domestic microwave oven was used for all the experiments. The average bulk temperature at the end of the reaction was measured by inserting a thermometer in the reaction mixture. All the experiments were done with water as a solvent and at temperatures less than 100 °C. For all the MW powers studied, the exposure time was varied from 0.33 min to 1.66 min but for grafting using the redox system and catalyst at 80% microwave power, the minimum exposure time used was 0.22 min. This allowed temperatures ~60 °C to be obtained compared with 73 °C for 0.33 min exposure. I.R. spectra were recorded on a Brucker Vector-22 Infra red spectrophotometer using KBr pellets. %*N* was determined by EA 1110 CHNS-O analyzer (Thermoquest CE Instrument). Acrylamide (E.Merck) was recrystallized twice from methanol (GR) and dried under vacuum. Ascorbic acid and Potassium persulfate (BDH, Analar Grade) were used without further purification. $AgNO_3$ (Merck) was used as catalyst. Commercial GG was purified further before use. ^1H spectra were recorded on a Jeol 400 MHz FT NMR in D_2O. X-ray diffraction (XRD) was carried out on Isodebeyxlex 2002 X-ray powder diffractometer and TGA was carried out on Perkin Elmer Pyris 6TGA in N_2 atmosphere. Samples with highest %*G* was used for the XRD and TGA studies

The percentage and efficiency of grafting were calculated according to Kojima et al. (Bajpai & Rai, 1988).

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

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

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

2.1. Purification of the guar gum

The commercial GG was purified (Singh et al., 2003) through 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 added to 1 M acetic acid stirred for 8 h, centrifuged and precipitated with ethanol. It was washed with 70, 80, 90 and 95% ethanol. The sample was finally purified by dialysis and filtration through various 0.45 μm millipore membranes.

2.2. Grafting in aqueous medium under MW irradiation with redox initiator

A solution (total volume 25 ml) of GG (0.1 g), AA (16×10^{-2} mol/l), $AgNO_3$ (8.0×10^{-5} mol/l), $K_2S_2O_8$ (1×10^{-3} mol/l), and ascorbic acid (22×10^{-3} mol/l) in water in a 150 ml flask was kept inside a domestic MW oven, and subjected to irradiation to different MW power for different exposure time G-g-PAA was separated (Bajpai et al., 1990) from PAA by precipitating the reaction mixture with methanol: water (7:3) in which the homopolymer dissolves. Grafted gum was repeatedly washed with methanol: water (7:3) and dried. %*G* and %*E* were calculated.

Grafting yield in potassium persulphate/ascorbic acid initiated graft copolymerization of AA with GG, under MW was found to be highest at 80% microwave power for exposure time of 0.22 min and temperatures of 60 °C.

2.3. Grafting in aqueous medium without redox system and catalyst under MW

A solution (total volume 25 ml) of GG (0.1 g) and AA (16×10^{-2} mol/l) in water was irradiated in a domestic MW oven in a 150 ml flask The reaction was repeated with different MW powers and exposure time. The G-g-PAA was separated as described above. In the absence of initiators and catalyst the maximum grafting was observed at 70% MW power at temperature 63 °C.

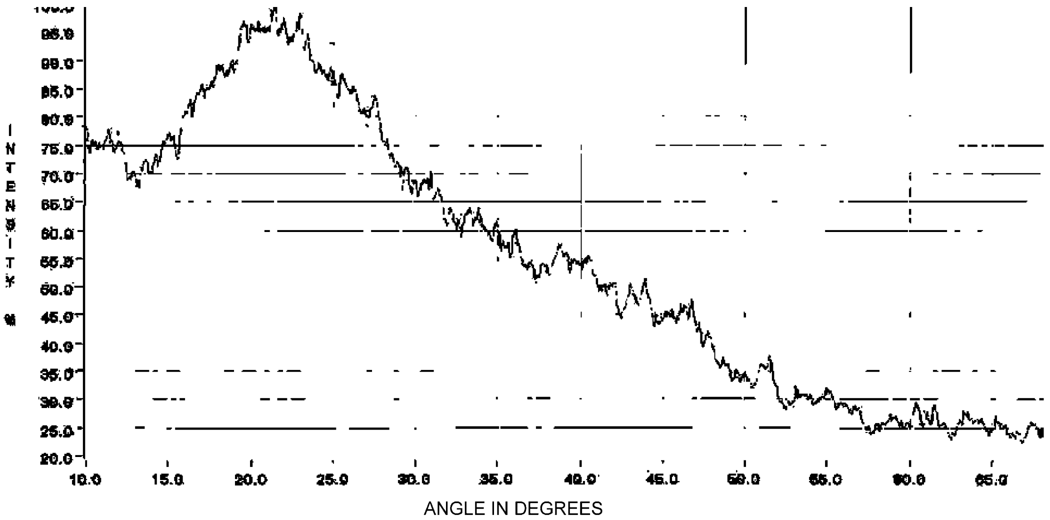
2.4. Grafting in aqueous medium on thermostatic water bath

A solution (total volume 25 ml) of GG (0.1 g), AA (16×10^{-2} mol/l), $AgNO_3$ (8.0×10^{-5} mol/l), and ascorbic acid (22×10^{-3} mol/l) in water in a 150 ml conical flask was thermostated at a temperature of 35.0 ± 0.2 °C After 30 min $K_2S_2O_8$ (1×10^{-3} mol/l), was added, and this time of addition of persulphate was taken as zero time. The reaction was allowed to continue for 1 h. Separation of G-g-PAA from AA was done as described above. (%*G*130; %*E*45.61). The experiment was repeated at 60°. At 60 °C % grafting was found to be 140% and % efficiency 49.12%.

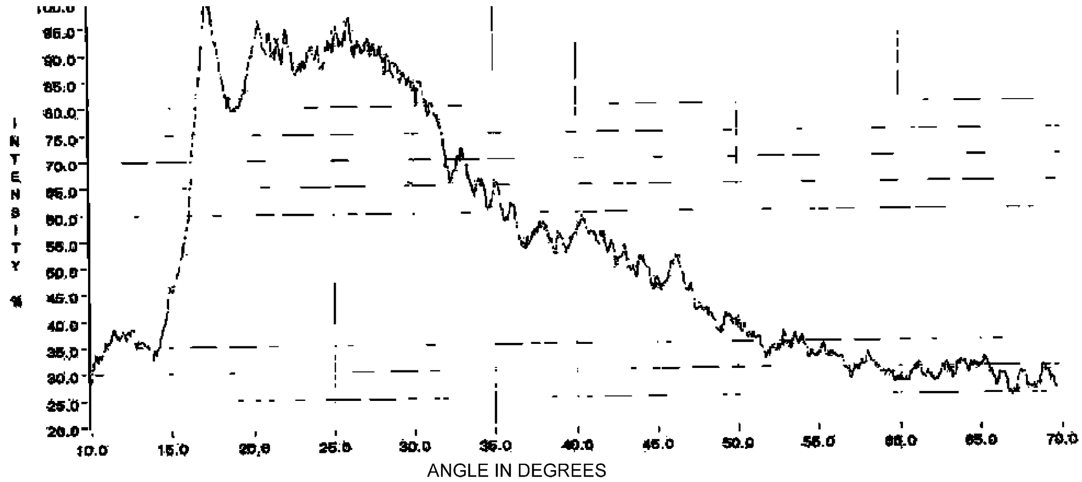
3. Results and discussion

Under MW irradiation, grafting of the PAA in aqueous medium was found to take place in the absence of any redox system and catalyst, with yields comparable to the thermal grafting (Bajpai et al., 1990) with potassium persulphate/ascorbic acid in the presence of Ag^+ and atmospheric oxygen When potassium persulphate/ascorbic acid system was used in conjunction with the MW, %*G* was 190% in only 0.22 min. Thus in the grafting under MW, the use of expensive catalyst and redox system can be avoided and grafting takes place in an environmental friendly manner in an aqueous medium where no catalyst and redox system is required. Conventionally it was not possible to graft PAA on to GG in absence of initiator even when the temperature was 100 °C so the effect observed must be due to MW produced radicals.

G-g-PAA was characterized by infrared spectroscopy and proton NMR [22] and CHN analysis. Infrared spectrum of pure guar gum has a broad strong band at 3410 cm^{-1}, a band at 2900 cm^{-1} indicating C–H linkages while IR spectrum of G-g-PAA has an absorption peak at 1682.32 cm^{-1} for $>$C=O stretching, N–H stretching peaks at 3363 and 3210 cm^{-1} and C–N stretching at 1455 cm^{-1}. A physical blend of guar gum and PAA after selective removal of PAA with methanol: water (7:3) showed no absorption at 1680, 3350 and 3170 cm^{-1}. This substantiates the formation of the graft copolymer. ^{1}H NMR of the pure gum showed a peak at δ 4.67(s), anomeric protons, and at δ 3.5–3.9 (m) due to other sugar protons while the grafted gum showed a peak at δ 4.65 (s) due to anomeric protons (N–H protons cannot be observed due to deuterium exchange) and at δ 2.0–2.1 and δ 1.5–1.6 (due to protons at grafted chains of PAA on the GG backbone) indicating the presence of PAA chain attached to the GG. %*N* shows that the grafting in the absence of redox system is uneven. MW assisted grafting, both in presence and in absence of radical initiators and catalyst, results into the copolymers with lower %*N* in comparison to the polymer obtained with conventional thermal grafting indicating that the grafted chains in the former are either of smaller size or



XRD of pure guar gum



XRD of MW Grafted G-g-PAA (synthesized with 70% MW power in 0.33 minutes at 63° without radical initiator and/or catalyst)

Fig. 1. XRD of pure guar gum. XRD of MW Grafted G-g-PAA (synthesized with 70% MW power in 0.33 min at 63° without radical initiator and/or catalyst).

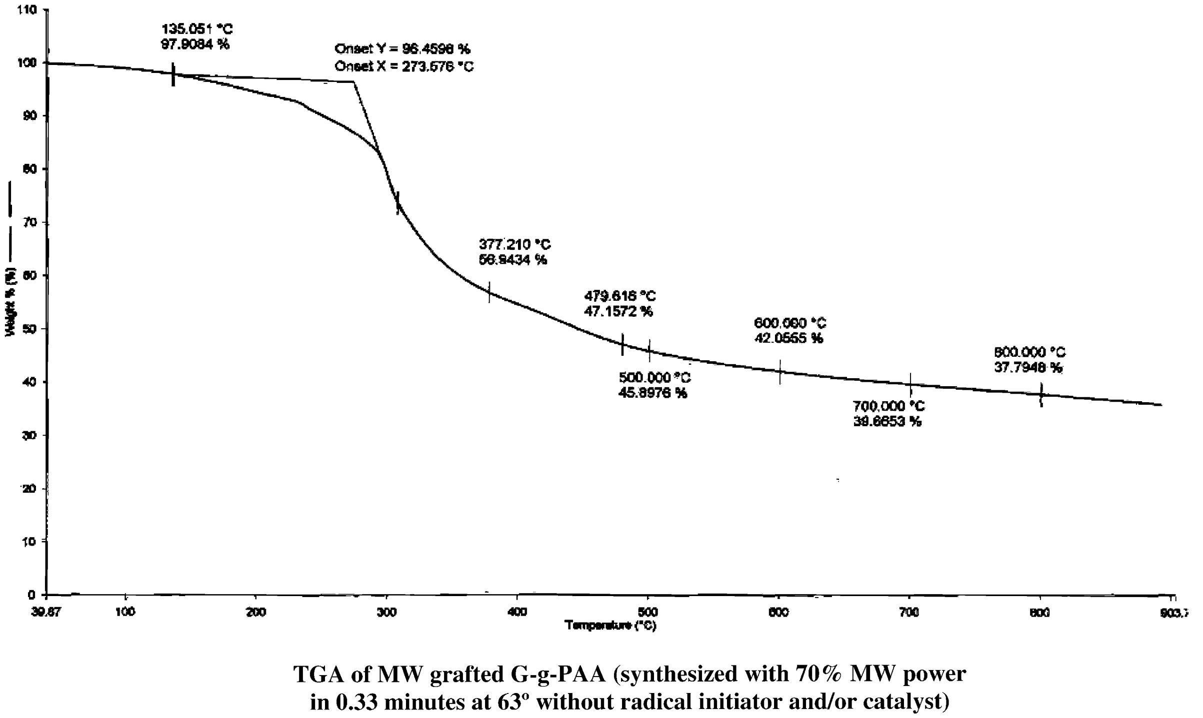


Fig. 2. TGA of MW grafted G-g-PAA (synthesized with 70% MW power in 0.33 min at 63° without radical initiator and/or catalyst).

more widely scattered on to the GG backbone. XRD of GG is compared with the MW grafted gum (Fig. 1). XRD spectra of the grafted gum showed an additional sharp peak corresponding to the crystallinity of grafted PAA chain on guar gum backbone. The other broader peak indicates the decreased crystallinity of pure GG after grafting. The TGA of the grafted gum (Fig. 2) shows that decomposition onsets at 273.5 °C indicating its high thermal resistivity.

%*G* increases with the increase of MW power and exposure time in the beginning but when MW power was more than 70% (in absence of initiator and catalyst) and more than 80% (in presence of initiator) used grafting yields are lowered indicating that higher microwave radiation promotes homopolymerization more, than the graft co-polymerization and due to formation of more homopolymer the yield of grafted gum is lowered. When the temperature is in the range of 60–65°, the %*G* observed was maximum and any further increase in temperature lowered the grafting yield indicating side reactions at higher temperatures. In the absence of the redox system and catalyst %*E* was maximum (42.10%) under 70% microwave power and at temperature 63 °C. While the optimal grafting (grafting efficiency 66.66%) in presence of redox system and catalyst could be achieved under 80% MW power (exposure time 0.22 min and temperature 60 °C). Thus grafting of AA on to the GG under MW irradiation can be done without using any redox system and catalyst. Grafting under MW irradiation with and without redox system and catalyst are compared with conventional thermal grafting in Table 1.

Under MW, in presence of catalyst and redox system yields are higher than conventional thermal grafting (which require redox system and catalysts) and reactions are performed in much shorter reaction times (Table 2).

4. Mechanism

With the persulphate/Ascorbic acid redox system the mechanism has been described (Bajpai & Jain, 1993). A plausible mechanism for the grafting under MW in absence of initiators is proposed below.

GG molecule is quite large but relatively rigid molecule with pendent –OH groups under MW irradiation. –OH groups attached to large GG molecule can behave as if were anchored to an immobile raft and its immobile localized rotations (Gabriel et al., 1998) will occur in the MW region and resulting dielectric heating of the GG molecule may result in an enhancement of reaction rates specifically at these groups. The dielectric heating will involve rapid

Table 1
Optimum conditions used to get maximum %*G*

	Conven. method with redox system and catalyst	Under MW presence of redox system and catalyst	Under MW absence of redox system and catalyst
% grafting	140	190	120
% Efficiency	49.12	66.66	42.10
Microwave power	–	80%	70%
Temperature	60 °C	60 °C	63 °C
Time	80 min	0.22 min	0.33 min
%*N*	4.98	3.26	2.47

Table 2
Showing the variation of temperature and grafting efficiency with change in MW power and exposure time in presence and absence of redox system and catalyst

Sl. No.	% MW	Exposure time in min	Without redox system and catalyst				With redox system and catalyst			
			Temp (°C)	Yield	*%G*	*%E*	Temp (°C)	Yield	*%G*	*%E*
1	50%	0.33	60	210	110	38.59	65	105	5	1.75
		0.50	62	215	115	40.35	70	115	15	5.26
		0.66	70	180	80	28.07	92	132	32	11.23
		1.00	72	182	82	28.77	96	140	40	14.03
		1.33	85	184	84	29.47	98	150	50	17.54
		1.66	95	190	90	31.57	98	150	50	17.54
2	70%	0.33	63	220	120	42.10	72	132	32	11.22
		0.50	75	190	90	31.57	82	150	50	17.54
		0.66	85	198	98	34.38	96	178	78	27.37
		1.00	95	200	100	35.08	98	185	85	29.82
		1.33	100	202	102	35.78	100	190	90	31.58
		1.66	100	202	102	35.78	100	190	90	31.58
3	80%	0.33	66	200	100	35.08	73	230	130	45.61
		0.50	77	183	83	29.12	85	230	130	45.61
		0.66	90	185	85	29.82	98	242	142	49.82
		1.00	98	190	90	31.57	100	252	152	53.33
		1.33	100	192	92	32.28	100	281	181	63.50
		1.66	100	192	92	32.28	100	282	182	63.85
4	90%	0.33	75	160	60	21.05	81	180	80	28.07
		0.50	90	165	65	22.80	94	182	82	28.77
		0.66	92	168	68	23.85	95	190	90	31.57
		1.00	98	170	70	24.56	100	190	90	31.57
		1.33	100	172	72	25.26	100	210	110	38.59
		1.66	100	175	75	26.31	100	217	117	41.05
5	100%	0.33	83	155	55	19.29	85	168	68	23.85
		0.50	90	165	65	22.80	95	170	70	24.56
		0.66	95	170	70	24.56	98	192	82	28.77
		1.00	100	175	75	26.31	100	216	90	31.57
		1.33	100	175	75	26.31	100	220	100	35.08
		1.66	100	176	76	26.66	100	222	110	38.59

energy transfer from these groups to neighboring molecules (AA and water) as it is not possible to store the energy in a specific part of the molecule. In the GG molecule there are a large numbers of OH groups so the taken up energy is expected to be high and may result into cleavage of this bond. Further MW are reported to have the special effect (Galema, 1997) of lowering of Gibbs energy of activation of the reactions In view of the above two effects it is proposed that −OH groups of the GG being polar will absorb MW energy and will cleave generating monomer free radicals and macroradicals. The Scheme is given below.

$$\mathrm{GOH} + \mathrm{M} \xrightarrow{\mathrm{MW}} \mathrm{GO}^{\cdot} + \mathrm{M}^{\cdot} \qquad (1)$$

$$\mathrm{GO}^{\cdot} + \mathrm{M} \rightarrow \mathrm{GOM}^{\cdot} \qquad (2)$$

$$\mathrm{GOM}^{\cdot} + \mathrm{M} \rightarrow \mathrm{GOMM}^{\cdot} \qquad (3)$$

$$\mathrm{GOMM}^{\cdot}_{n-1} + \mathrm{M} \rightarrow \mathrm{GOM}^{\cdot}_{n} \qquad (4)$$

$$\mathrm{GOM}^{\cdot}_{n} + \mathrm{GOM}^{\cdot}_{n} \rightarrow \text{Grafted polymer} \qquad (5)$$

$$\mathrm{M}^{\cdot} + \mathrm{M} \rightarrow \mathrm{MM}^{\cdot} \qquad (6)$$

$$\mathrm{M}^{\cdot}_{n-1} + \mathrm{M} \rightarrow \mathrm{M}^{\cdot}_{n} \qquad (7)$$

$$\mathrm{M}^{\cdot}_{n} + \mathrm{GOH} \rightarrow \mathrm{GO}^{\cdot} + \mathrm{M}_{n}\mathrm{H}\ \text{(homopolymer)} \qquad (8)$$

Where GOH stands for Guar gum, M stands for acrylamide, MW for microwave irradiation.

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