Grafting of Polyacrylonitrile onto Guar Gum Under Microwave Irradiation

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ABSTRACT: Using microwave (MW) irradiation grafting of polyacrylonitrile (PAN) onto guar gum in water was done without using any radical initiator or catalyst within a very short reaction time. The extent of grafting could be adjusted by controlling the reaction conditions and maximum percentage grafting (%G) of about 188% was obtained under optimum conditions in 1.66 min. The average molecular weight of the grafted PAN chains and water-retention power of the alkali hydrolyzed MW-grafted gums were also determined and compared with those of the conventionally synthesized (cs) graft copolymer. A representative MW-grafted copolymer, guar-g-polyacrylonitrile was characterized by IR, NMR, XRD, TGA, and elemental analysis. A plausible mechanism for the grafting under MW was proposed. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 1569–1575, 2004

Key words: graft copolymer; guar gum; acrylonitrile; microwave irradiation; water retention

INTRODUCTION

Guar gum (GG) is an edible carbohydrate polymer[1] found in the seeds of *Cyanaposis tetragonolobus*. It is a nonionic, branched-chain polymer, consisting of a 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. GG is a cold-water[2] swelling polymer and is reported to be one of the most highly efficient water thickeners. It is routinely used as a dispersion agent, as a viscosity builder, and water binder in many industries such as mining, textiles, explosives, paper, and petroleum, for example. Although an advantageous property, this viscosity is difficult to control because of its quick biodegradation,[3] which is why it is rarely used in its natural form.

Modification by grafting of water-soluble vinyl monomers onto GG results in the retention of desirable properties and incorporation of favorable properties. Singh and coworkers[4] found that graft copolymers of guar/xanthan gum/starch exhibit much better flocculating characteristics than those of conventional polysaccharides,[5] alone and with some of the synthetic polymer–based flocculating agents.

Lokhande[6] prepared water supersorbent guar-modified polymers by graft copolymerization of acrylonitrile onto GG through γ-radiation. Conventionally, polyacrylonitrile (PAN) has been grafted onto GG using various redox systems.[7–9] Concurrent homopolymer formation is the main constraint in graft copolymerization, which leads to a low grafting yield. Microwave (MW) irradiation,[10] as efficient thermal energy, is becoming the standard technique in various fields of chemistry. Grafting of butylacrylate,[11] acrylic acid,[12] and acrylonitrile[13] onto the starch; of acrylamide onto linear low-density polyethylene (LLDPE) films[14]; and of butyl methacrylate onto wool fibers[15] was studied recently under MW irradiation using redox initiators. Yields were high and the grafting could be achieved within a very short time. Polymerization of methylmethacrylate with low concentration of initiating system under MW irradiation was also reported very recently.[16]

Because MW irradiation is reported to generate free radicals we were prompted to study whether grafting is possible without using any initiator or catalyst under MW irradiation. Somewhat surprisingly, we successfully were able to achieve grafting of PAN onto the GG under MW irradiation without the use of any radical initiators or catalyst.

EXPERIMENTAL

A Kenstar (Model No. MOW 9811, 1200 W, Aurangabad, India) 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, and at all times it was less than 100°C because water was chosen as the solvent for the study. Infrared (IR) spectra were recorded on a Brucker Vector-22 infrared spectrophotometer (Brucker, Rheinstetten, Germany) using KBr pellets. Elemental analysis was carried out on an EA 1110 CHNSO analyzer (Thermoquest CE Instruments). Acrylonitrile (E. Merck, Darmstadt, Germany) was distilled in a stream of nitrogen before use. Ascorbic acid and potassium persulfate (analar grade; BDH, Poole, UK) were used without further purification. Commercial GG was purified further before use. ^{1}H spectra were recorded on a JEOL 400-MHz FT NMR (JEOL, Tokyo, Japan) in D_2O. A Ubbelhode viscometer (Cannon–Ubbelhode, State College, PA) was used for the viscocity measurements. X-ray diffraction (XRD) was carried out on an Isodebeyxlex 2002 X-ray powder diffractometer (Rich Siefert & Co., Germany) and TGA was carried out on Perkin–Elmer Pyris 6TGA (Perkin Elmer Cetus Instruments, Norwalk, CT) in N_2 atmosphere.

The percentage and efficiency of grafting (%G and %E, respectively) were calculated according to Kojima et al.[19]:

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

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

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

Water absorption[20] was measured in terms expressed in the following equation:

$$C_{WA} \text{ (g/g)} = \frac{W_1 + W_2}{W_1} \qquad (3)$$

where C_{WA} is the water absorption capacity, and W_1 and W_2 represent the mass of the dried powdered sample and amount of water absorbed, respectively.

% Add on[21] was calculated using eq. (4):

$$\% \text{ Add on} = \frac{W_1}{W_2} \times 100 \qquad (4)$$

where W_1 is the weight of synthetic polymer and W_2 is the total weight of graft copolymer.

Purification of the guar gum

Commercial GG was purified[22] 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 a standard barium hydroxide solution. The complex was separated by centrifugation and taken in 1M 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 (Millipore, Milford, MA).

Grafting by the conventional method[9]

Guar gum (0.1 g), acrylonitrile (26×10^{-2} mol/L), and ascorbic acid (2.3×10^{-2} mol/L) (in water) were charged to a 150-mL flask and thermostated at 35 ± 0.2°C. After 30 min potassium persulfate (10×10^{-3} mol/L) was added to the mixture. The total volume of the reaction mixture was kept to 25 mL and grafting was allowed for 1 h. Guar-g-polyacrylonitrile (G-g-PAN) was separated from PAN (homopolymer) by pouring the reaction mixture into an excess quantity of DMF.

Grafting under microwave irradiation
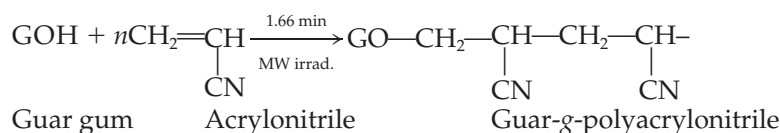
GG (0.1 g) and acrylonitrile (26×10^{-2} mol/L) were charged with 25-mL water to a 150-mL flask and irradiated in a domestic MW oven. The reaction was repeated with different monomer concentrations, polymer concentrations, MW power levels, and exposure times. G-g-PAN was separated[9] from PAN as described above. The grafted gum was repeatedly washed with DMF and dried. %G and %E values were calculated. Optimal grafting was observed at full MW power at a temperature of 97°C within 1.66 min (Table I).

Under MW irradiation (in the absence of catalyst or redox system) yields were better than those obtained by conventional thermal grafting[9] (which require a redox system and catalysts) and reactions are completed in much shorter reaction times. The results with

TABLE I
Variation of Grafting Efficiency with Change in Microwave Power and Exposure Time

Sample	% MW	Exposure time (min)	T (°C)	Yield	%G	%E
			Without redox system and catalyst			
1	50	0.33	62	132	32	9.28
		1.0	81	140	40	11.58
		1.66	97	167	67	19.42
2	70	0.33	78	142	42	12.17
		1.00	92	198	98	28.41
		1.66	97	226	126	36.52
3	80	0.33	84	154	54	15.65
		1.00	97	227	127	36.81
		1.66	97	235	135	39.13
4	90	0.33	78	162	62	17.97
		1.00	95	234	134	38.84
		1.66	97	252	152	44.06
5	100	0.33	82	183	83	24.06
		1.00	95	235	135	39.13
		1.66	97	288	188	54.49

optimal grafting yields under MW are compared with those of the conventional method in Table II.

Molecular weight of grafted PAN chains

Homopolymer-free graft copolymer samples were hydrolyzed in 2M HCl for 2 h to depolymerize the polysaccharide chains. The residue, consisting mainly of PAN chains, was washed with water and ethanol, dried in air, and weighed. (% Add on was calculated by the weight loss upon hydrolysis.) The PAN chains were extracted for 24 h at 20°C in DMF. After filtration, the PAN solutions were used for molecular weight determination by measuring the viscosities at different concentrations. The M_n values were calculated from the following relation[23]:

$$[\eta] = 3.92 \times 10^{-4} \times \bar{M}_n^{0.75} \qquad (5)$$

Viscosity measurements

Viscosity measurements[24] of polymer solutions were measured in DMF solutions at 30°C. The flow time was measured for solutions at five different concentrations. The intrinsic viscosity was calculated by plotting η_{sp} versus C and η_{inh} versus C and then taking the common intercept at $C = 0$ of the best-fitted straight line through the two sets of points. Here C represents polymer concentrations in g/dL. The η_{sp} and η_{inh} are specific and inherent viscosities and were calculated from the relation $\eta_{sp} = \eta_{rel} - 1$ and $\eta_{inh} = \ln \eta_{rel}/C \approx t/t_0$.

Hydrolysis in aqueous alkali

Samples of the grafted GG were hydrolyzed[19] in aqueous alkali. Grafted samples (2 g, on dry basis) were dispersed in 1% NaOH at 100°C for 1.5 h. After hydrolysis the samples were precipitated in 600 mL methanol, washed with methanol and ethanol, dried, and weighed.

Water retention of the hydrolyzed samples

The alkali-hydrolyzed samples (0.5 g, on dry basis) were swollen[19] 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

TABLE II
Comparison of Guar-*g*-PAN Synthesized Conventionally and by Microwave Power

Variable	Conventions method With redox system and catalyst	Under MW in absence of redox system and catalyst
% Grafting	177	188
% Efficiency	51.30	54.49
Microwave power	—	100%
Temperature	35°C	97°C
Time	90 min	1.66 min
%N	9.65%	11.9%
% Add on	32%	71%
Intrinsic viscosity of the grafted PAN chain solutions	0.75 dL/g	1.75 dL/g
Average molecular weight of the grafted chains	2.89×10^2	5.46×10^2
Water absorption capacity of alkali hydrolyzed grafted gums (g/g)	2.90	6.22
Flame resistance	Resist flame for 5 s, swell, and burn completely in 25 s	Resist flame for 20 s, swell, and burn completely in 60 s

Sample	Monomer concentration	%G
1	8.8×10^{-2}	125
2	10×10^{-2}	140
3	12×10^{-2}	153
4	14×10^{-2}	169
5	18×10^{-2}	172
5	20×10^{-2}	178
6	26×10^{-2}	188

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.

RESULTS AND DISCUSSION

Under MW irradiation, PAN could be efficiently grafted onto the GG using water as a solvent (aqueous medium), without using any redox system and catalyst. Furthermore, the MW method was much faster than the conventional thermal grafting method.[9] Although without initiator and catalyst grafting could not be achieved under similar reaction conditions by thermal heating, even when the reaction temperature was raised to 100°C, grafting under microwave irradiation thus cannot be merely ascribed to the thermal effect. %G and %E were found to increase as the MW power and exposure time were increased (Table I) and maximum grafting could be achieved under full MW power after an exposure time of 1.66 min. The rate of grafting under MW was found to increase with the concentration of the monomer acrylonitrile in the range of 8.8 to 26.0×10^{-2} M/L. The maximum %G achieved was 188% when the other parameters were kept constant, whereas the maximum %G reported for the conventional method by Bajpai et al.[9] was 177% at a fixed concentration of persulfate (10×10^{-3} mol/L) and ascorbic acid (2.3×10^{-2} mol/L), conducted at varying concentrations of acrylonitrile in the range of $8.8–26 \times 10^{-2}$ (Table III).
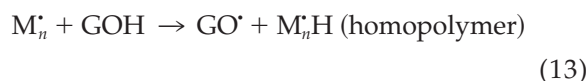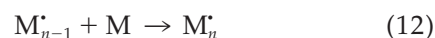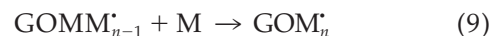
The increase in the rate and efficiency of grafting with the increase in acrylonitrile concentration may be attributed to two reasons: (1) the formation of more $M_n^{\cdot}$ radicals generating more grafting sites and (2) the availability of extra monomer molecule for grafting. The effect of concentration of the GG was studied in the range 0.1–0.4 g, with other parameters kept constant. It was found that both %G and %E decrease with the increase in GG concentration in the studied range, which may be attributed to the increase in viscosity of the medium, thus hindering the normal graft copoly-

merization. G-*g*-PAN was characterized by using XRD, IR, ^{1}H-NMR,[17] and elemental analysis.

Mechanism

Grafting in the absence of any initiators or catalyst under MW radiation can be explained by the following proposed plausible mechanism.

The GG molecule is quite a large molecule with pendent –OH groups. –OH groups attached to the large GG molecule may behave as though they were anchored to an immobile raft. Its localized rotations[18] therefore will be observed in the microwave region and the consequent dielectric heating of the GG molecule may result in an enhancement of reaction rates specifically at these groups. The dielectric heating will involve rapid energy transfer from these groups to neighboring molecules (acrylonitrile and water) because it is not possible to store the energy in a specific part of the molecule. In the GG molecules there are large numbers of –OH groups, so this energy amount is expected to be substantial and this may be responsible for breaking –OH bonds. Moreover, MW irradiation is also reported to have special effects[10] of lowering the Gibbs energy of activation of the reactions. In view of the above two effects a plausible free-radical mechanism for grafting under microwave irradiation was proposed. The –OH groups of the GG, because they are polar, will absorb MW energy and will cleave generating monomer free radicals and macroradicals, according to the following series of reactions:

$$\text{GOH} + \text{M} \xrightarrow{\text{MW}} \text{GO}^{\cdot} + \text{M}^{\cdot} \qquad (6)$$

$$\text{GO}^{\cdot} + \text{M} \rightarrow \text{GOM}^{\cdot} \qquad (7)$$

$$\text{GOM}^{\cdot} + \text{M} \rightarrow \text{GOMM}^{\cdot} \qquad (8)$$

$$\text{GOMM}_{n-1}^{\cdot} + \text{M} \rightarrow \text{GOM}_n^{\cdot} \qquad (9)$$

$$\text{GOM}_n^{\cdot} + \text{GOM}_n^{\cdot} \rightarrow \text{Grafted polymer} \qquad (10)$$

$$\text{M}^{\cdot} + \text{M} \rightarrow \text{MM}^{\cdot} \qquad (11)$$

$$\text{M}_{n-1}^{\cdot} + \text{M} \rightarrow \text{M}_n^{\cdot} \qquad (12)$$

$$\text{M}_n^{\cdot} + \text{GOH} \rightarrow \text{GO}^{\cdot} + \text{M}_n^{\cdot}\text{H (homopolymer)} \qquad (13)$$

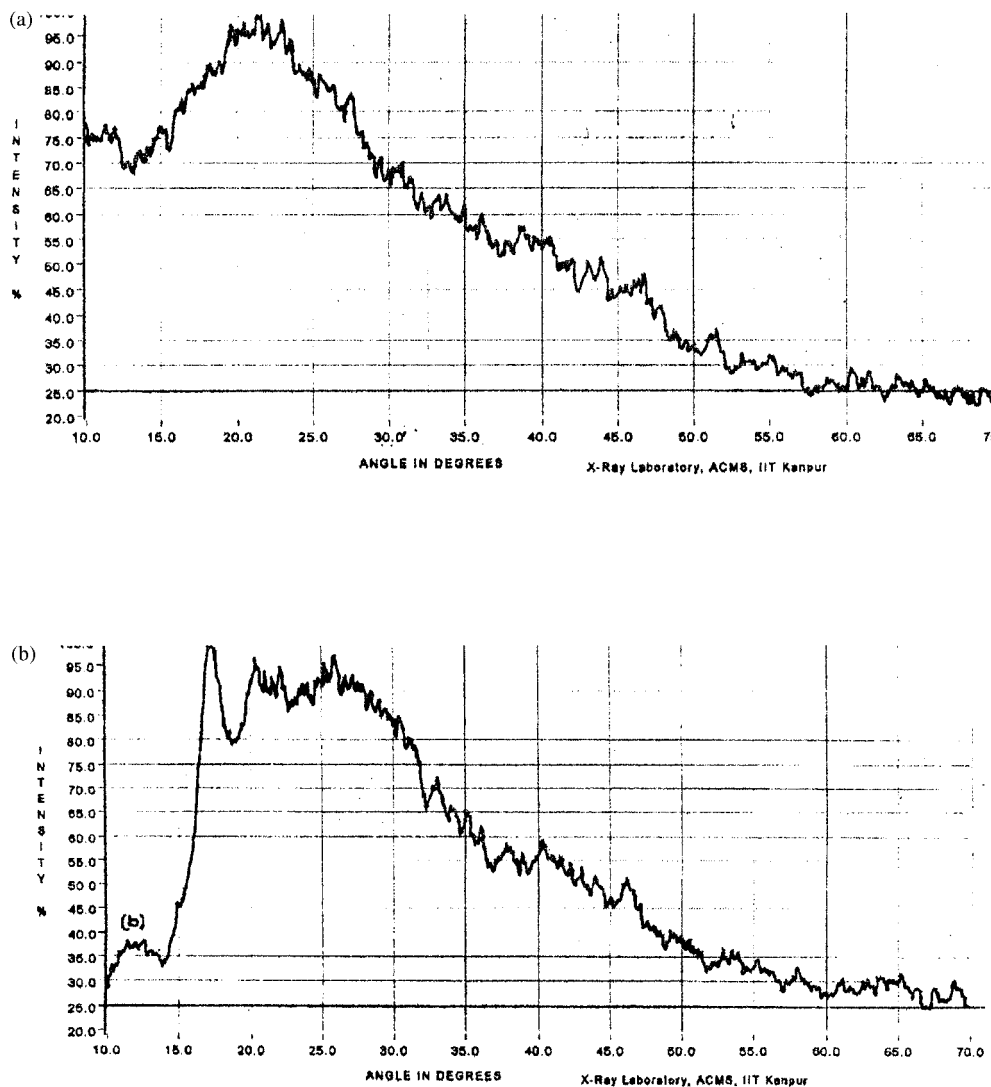where GOH represents guar gum, M represents acrylonitrile, and MW is microwave irradiation.

Figure 1 XRD spectra of (a) pure guar gum and (b) guar-*g*-PAN.

Characterization of the grafted gum

XRD spectra of GG compared with those of the MW-grafted gum are shown in Figure 1(a) and (b), respectively. The XRD spectrum of the grafted gum showed an additional sharp peak corresponding to the crystallinity of grafted PAN on the guar backbone. The other broader peak indicates the decreased crystallinity of pure GG after grafting.

The IR spectrum of pure GG has a broad, strong band at 3410 cm^{-1} and a band at 2900 cm^{-1}, indicating C—H linkages, whereas the IR spectrum of MW-grafted guar has strong absorption peaks at 2244 cm^{-1} for –CN stretching and CH$_2$ deformation vibration at 1451 cm^{-1} (Fig. 2). The physical blend of GG and PAN after selective removal of PAN with DMF showed no absorption in –CN stretching and the –CH$_2$ bending region. This substantiates the formation of the graft copolymer.

^{1}H-NMR analysis of the pure gum showed a peak at δ 4.67 (s) for anomeric hydrogens, and at δ 3.5–3.9 (m) attributed to sugar protons [Fig. 3(a)], whereas the MW-grafted gum showed a peak at δ 4.65 (s) attributed to anomeric protons (N—H protons cannot be observed because of deuterium exchange) and at δ 2.85 and δ 2.71 (attributed to protons at grafted chains of PAN on the guar gum backbone), indicating the presence of PAN, whereas no peak was observed in the δ 3.5–3.9 region [Fig. 3(b)].

Average molecular weights of PAN chains in CS-grafted gum and the MW-grafted GG were 2.89 × 10^2 and 5.46 × 10^2 g, respectively, as calculated by the viscosity method. Grafted gums after hydrolysis with alkali were tested for water retention. MW-grafted gum had a water absorption value of 6.22 g/g compared to 2.90 g/g for the CS-grafted samples. Thus, the increased degree of grafting (measured as % add-on) resulted in a pronounced increase in the water retention of the hydrolyzed samples. MW-grafted gums were observed to have more resistance to fire than the CS-grafted guar gum. TGA thermograms of the grafted gums (Fig. 4)
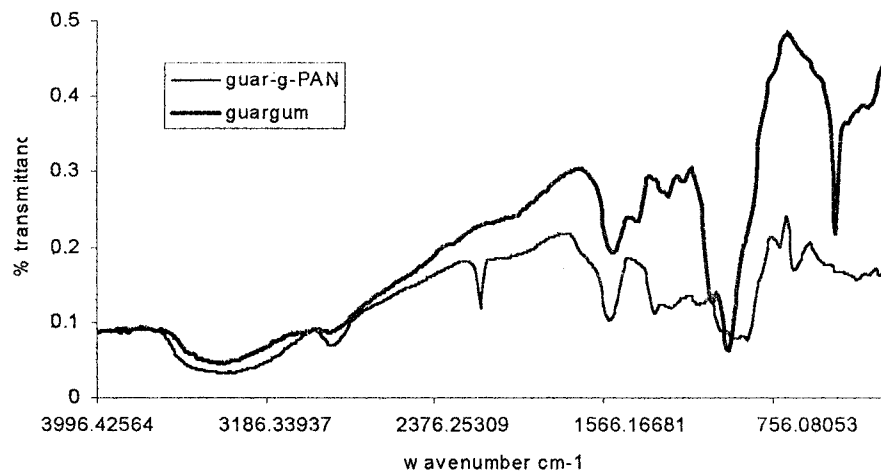
Infrared spectra of pure Guar gum and Guar-g-polyacrylonitrile

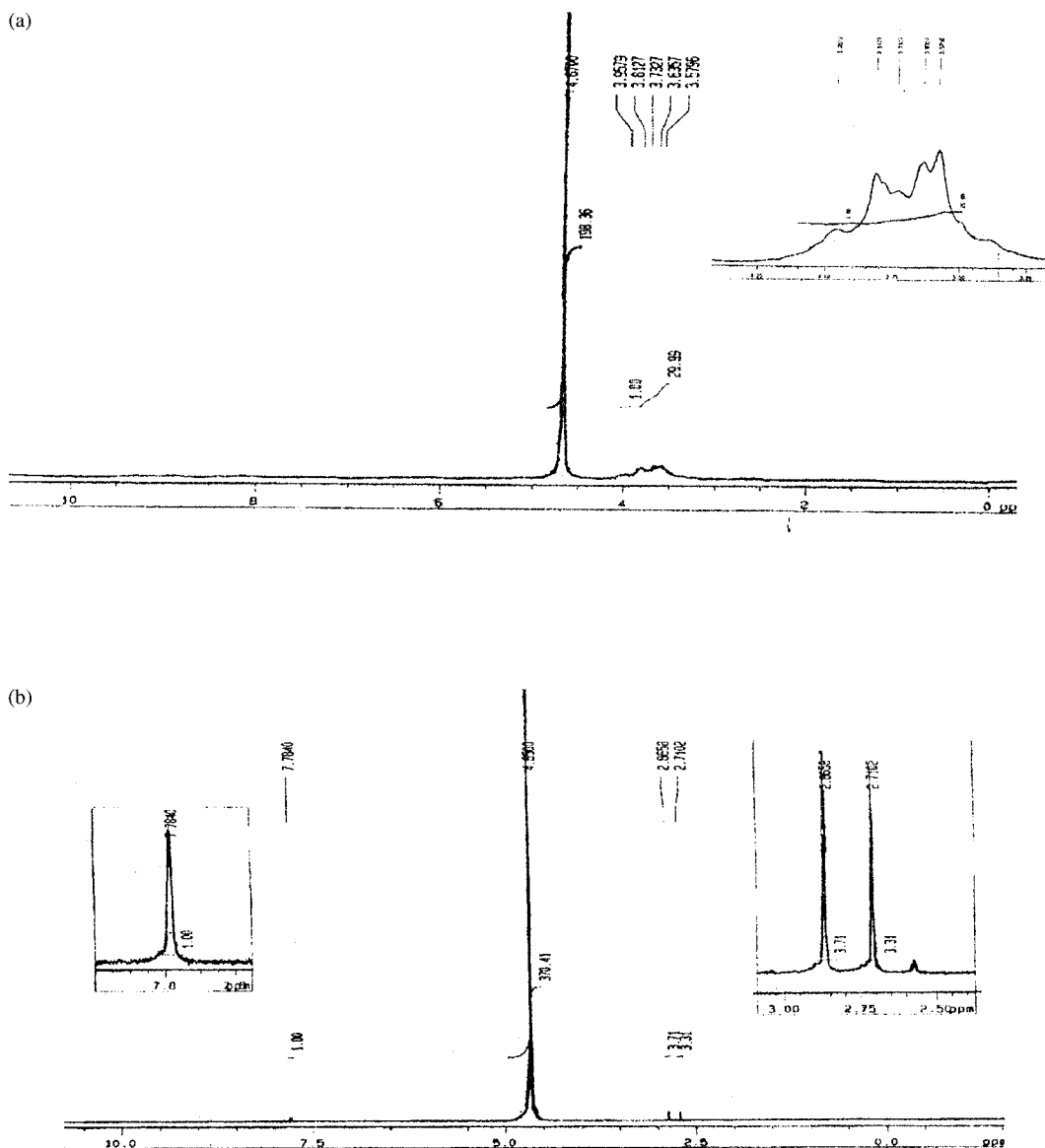**Figure 2**   Infrared spectra of pure guar gum and guar-*g*-PAN.

(a)

(b)

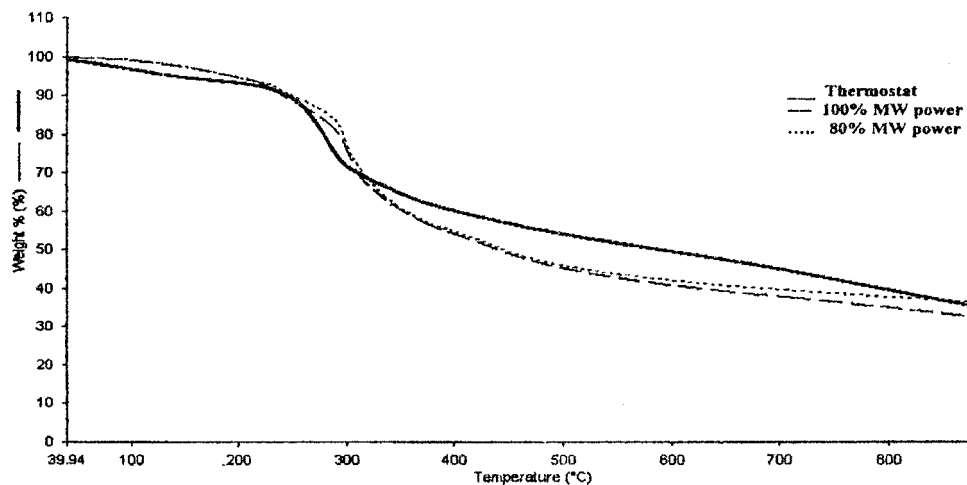**Figure 3**   ¹H-NMR of (a) pure guar gum and (b) guar-*g*-PAN.

Figure 4 TGA thermograms of guar-*g*-PAN synthesized by thermostat and MW.

show that the onset of decomposition is at 273.5°C in MW-synthesized gum, whereas in CS-grafted gum the onset of decomposition is at 249.4°C.

CONCLUSIONS

Using microwave, grafting of polyacrylonitrile onto guar gum could be achieved efficiently within a very short reaction time in the absence of any catalyst or redox initiators, whereas the conventional method not only requires redox initiator and catalyst but also takes a longer time and is relatively less efficient. Furthermore, the MW grafted sample on hydrolysis by the alkali yields a product with higher water-absorbing capacity (6.22 g/g) and higher flame resistance than that of the CS grafted GG, which may find better industrial applications. In efforts to work toward clean green chemistry, microwave can be a very useful tool for the synthesis of guar-*g*-PAN.

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