Modification of Guar Gum Through Grafting of 4-Vinyl Pyridine using Potassium Peroxymonosulphate/Ascorbic Acid Redox Pair

Abhishek Srivastava, Jasaswini Tripathy, Madan Mohan Mishra, Kunj Behari

Polymer Science Research Laboratory, Department of Chemistry, University of Allahabad, Allahabad 211002, India

ABSTRACT: In the present article, the graft copolymerization of 4-vinyl pyridine onto guar gum initiated by potassium peroxymonosulphate/ascorbic acid redox pair in an aqueous medium was studied gravimetrically under a nitrogen atmosphere. Grafting ratio, grafting efficiency, and add on increased on increasing the concentration of potassium peroxymonosulphate from 5.0×10^{-4} to 10×10^{-4} mol/L and ascorbic acid concentration from 0.4×10^{-3} to 2.0×10^{-3} mol/L. On increasing the hydrogen ion concentration from 2.5×10^{-3} to 10.0×10^{-3} mol/L, grafting ratio, efficiency, add on and conversion were increased. Maximum grafting was obtained when guar gum and monomer concentration were 1.0 g/L and 20.0×10^{-2} mol/L, respectively. An increase in temperature from 30 to 35°C increased the grafting ratio, but conversion and homopolymer decreased. The graft copolymers were characterized by IR spectroscopy and thermogravimetric analysis. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1353–1358, 2007

Key words: graft copolymerization; 4-vinyl pyridine; guar gum; redox pair

INTRODUCTION

The modification of natural polymers, by graft copolymerization, is an attractive and cost effective technique for the preparation of new biomaterials. This is a quite promising method for improving the potential applications by introduction of desired properties and thus enlarges the scope of abundantly available polysaccharides.

Guar gum is a naturally occurring polysaccharide of a D-galacto-D-mannoglycon. It is a linear β (1→4) mannose to which α (1→6) galactopyranoside single subunits are attached as the side chains.[1] The traditional role of seed galactomannans in industries has been as viscosity builder, and thus is widely used as thickening agent in food industries, as well as binder,[2,3] but in recent years guar gum has been explored for controlled drug release.[4] Its glycosylated derivative is found to possess cancer chemopreventive activities.[5]

Pyridine has wide industrial applications in organic synthesis by itself or in conjunction with other reagents. The presence of reactive pyridyl nitrogen on the repeating unit of poly (4-vinylpyridine) makes the polymer attractive for use as a reagent. Hallensheben and Wurm[6] demonstrated that poly vinyl pyridine could be used as HCl acceptor. Frechet et al.[7,8] have reported that different derivatives of poly(vinyl pyridine) could act as brominating, oxidizing, and reducing agents. Kawabata et al.[9] employed the chloride salt of poly(N-benzyl 4-vinyl pyridine) to remove viruses from water, while Rivas et al.[10] have applied poly(4-vinyl pyridine) hydrochloride in selective removal of heavy metal ions.

Prompted by the fascinating properties of 4-vinyl pyridine and guar gum, we grafted 4-vinyl pyridine on guar gum. The synthesized graft copolymer would be more environmental friendly and cost effective than poly (4-vinyl pyridine) and is expected to hold better properties of metal ion uptake, swelling capacity, and thermal stability than substrate.

EXPERIMENTAL

Materials

4-Vinyl pyridine (Aldrich) was distilled under reduced pressure at 14 mmHg in presence of N_2 atmosphere. Potassium peroxymonosulphate was received as a gift sample from DuPont USA. Other chemicals like methanol and H_2SO_4 (AnalaR grade) were purchased from Merck. The ascorbic acid (Sigma) was kept under nitrogen atmosphere to prevent aerial oxidation. Guar gum was received as a gift sample from Hindustan Gums and Chemicals, India.

Correspondence to: K. Behari (kunjbehari1234@rediffmail.com).

TABLE I
Effect of Peroxymonosulphate Concentration on
Grafting Parameters

$[HSO_5^-]$ $\times$ 10^4 mol/L	%G	%E	%A	%C	%H
5.0	336.1	35.7	77.0	43.8	64.3
6.0	506.9	40.8	80.6	48.5	59.2
10.0	521.0	47.4	83.8	51.1	52.6
15.0	445.7	39.2	81.7	63.9	60.8

[AA] = 4.0 $\times$ 10^{-3} mol/L, [4-vp] = 20.0 $\times$ 10^{-2} mol/L, [H^+] = 10.0 $\times$ 10^{-3} mol/L, [GOH]= 1.0 g/L, time = 120 min, temperature = 35°C.

Graft copolymerization

For each experiment, guar gum solution was prepared by slow addition of calculated amount of guar gum into a reactor containing triple distilled water. The calculated amounts of 4-vinyl pyridine, sulfuric acid and ascorbic acid were added in the same reactor and a slow stream of oxygen free nitrogen gas was passed for 30 min. A known amount of deoxygenated potassium peroxymonosulphate solution was added to initiate the reaction. The reaction was performed under a continuous flow of oxygen free nitrogen gas and fixed temperature (35°C). After the desired time period, the reaction was stopped by letting air into the reactor. The graft copolymer was precipitated by pouring the reaction mixture into methanol, so that grafted guar gum was precipitated and poly(4-vinyl pyridine) remained in the filtrate because poly (4-vinyl pyridine) is soluble in water. The precipitate of grafted guar gum was separated, washed with water several times to remove the any trace of homopolymer, and then the grafted sample was dried and weighed. The poly (4-vinyl pyridine) was precipitated according to the method of Mariya et al.[11]

RESULTS AND DISCUSSION

The graft copolymer was characterized according to Fanta's[12] definition:

$$\text{Grafting ratio } (\%G) = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\text{Grafting efficiency } (\%E) = \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100$$

$$\text{Add on } (\%A) = \frac{\text{Grafted polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Conversion } (\%C) = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Homopolymer } (\%H) = (100 - \%\text{Grafting efficiency})$$

TABLE II
Effect of Ascorbic Acid Concentration on
Grafting Parameters

[AA] $\times$ 10^3 mol/L	%G	%E	%A	%C	%H
0.4	307.5	35.7	75.4	38.3	64.3
2.0	560.9	52.9	84.8	49.3	47.1
4.0	521.0	47.4	83.8	51.1	52.6
8.0	260.5	13.7	72.2	88.2	86.3

[HSO_5^-] = 10.0 $\times$ 10^{-4} mol/L, [4-vp] = 20.0 $\times$ 10^{-2} mol/L, [H^+] 10.0 $\times$ 10^{-3} mol/L, [GOH] = 1.0 g/L, time = 120 min, temperature = 35°C.

The effect of potassium peroxymonosulphate, ascorbic acid, sulfuric acid, 4-vinyl pyridine, and guar gum along with time and temperature was studied in terms of grafting ratio, efficiency, add on, conversion and homopolymer.

Effect of peroxymonosulphate concentration

The effect of potassium peroxymonosulphate on graft copolymerization was studied by varying the concentration from 5.0 $\times$ 10^{-4} to 15.0 $\times$ 10^{-4} mol/L. It was observed that grafting ratio, efficiency and add on increased on increasing the concentration of peroxymonosulphate up to 10.0 $\times$ 10^{-4} mol/L (Table I), but decreased at higher concentrations. The increase in the grafting parameters from 5.0 $\times$ 10^{-4} to 10.0 $\times$ 10^{-4} mol/L might be attributed to the production of more •OH and AA• free radicals. These free radicals are produced by progressive oxidation of ascorbic acid by peroxymonosulphate. •OH and AA• radicals interact with the monomer and guar gum molecules to produce the monomeric and macro guar gum radicals, and these radicals were responsible for the propagation of growing grafted
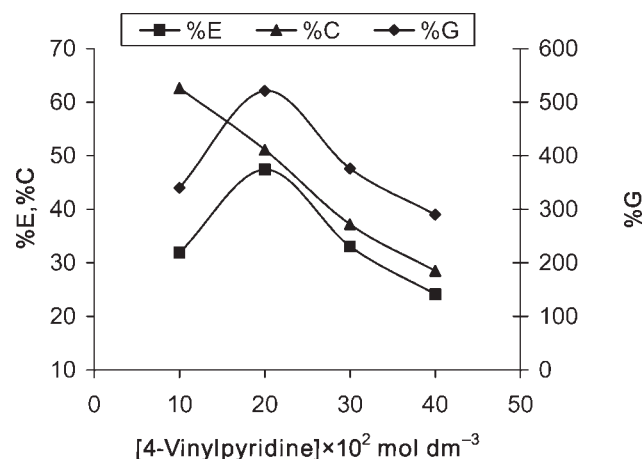
Figure 1 Effect of 4-vinyl pyridine concentration [HSO_5^-] = 10.0 $\times$ 10^{-4} mol/L; [AA] = 4.0 $\times$ 10^{-3} mol/L; [H^+] = 10.0 $\times$ 10^{-3} mol/L; [GOH] = 1.0 g/L; time = 120 min; temperature = 35°C.
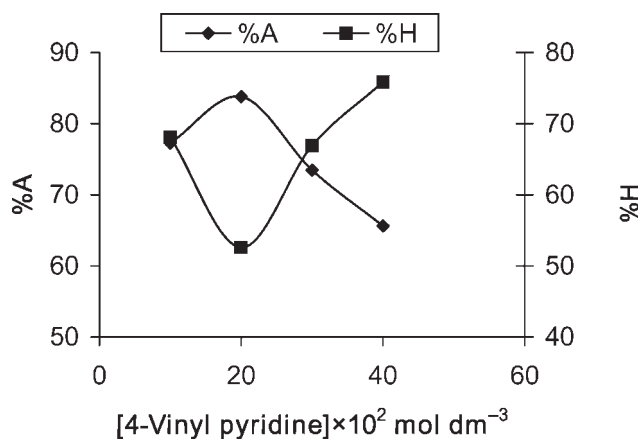
Figure 2 Effect of 4-vinyl pyridine concentration $[HSO_5^-]$ = 10.0×10^{-4} mol/L; [AA] = 4.0×10^{-3} mol/L; $[H^+]$ = 10.0×10^{-3} mol/L; [GOH] = 1.0 g/L; time = 120 min; temperature = 35°C.

chains. Retardation in grafting parameters beyond 10.0×10^{-4} mol/L concentration of peroxymonosulphate might be due to premature termination of the growing grafted chains.

Effect of ascorbic acid concentration

The results obtained by varying the concentration of ascorbic acid are summarized in Table II. The grafting ratio, efficiency and add on increased on increasing the concentration of ascorbic acid from 0.4 $\times 10^{-3}$ to 2.0×10^{-3} mol/L, and the increment might be due to increase in $^\bullet$OH and AA$^\bullet$ radicals concentration, which attack the guar gum molecule, resulting in more active sites at guar gum backbone where the addition of monomer takes place quickly. But on further increase in ascorbic acid concentration, i.e., beyond 2.0×10^{-3} mol/L, grafting ratio, add on and efficiency were decreased; however, conversion increased, which might be due to the formation of a high amount of homopolymer.
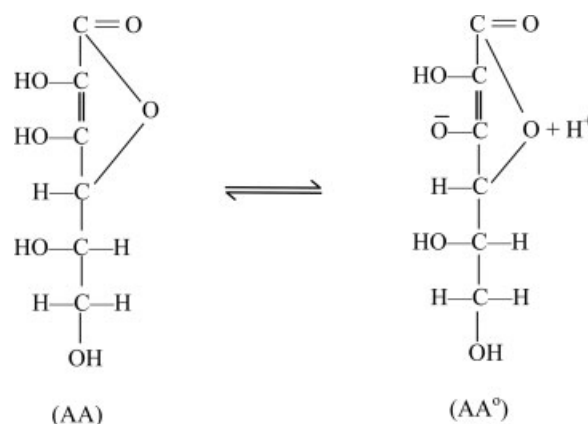
Effect of 4-vinyl pyridine concentration

The effect of monomer on reaction was studied by changing the concentration of 4-vinyl pyridine from 10.0×10^{-2} to 40×10^{-2} mol/L. The grafting ratio, add on and efficiency increased on increasing the concentration of 4-vinyl pyridine from 10.0×10^{-2} to 20.0×10^{-2} mol/L (Figs. 1 and 2), but grafting parameters decreased on further increasing the concentration of 4-vinyl pyridine up to 40.0×10^{-2} mol/L. However, maximum efficiency was observed when monomer concentration was 20.0×10^{-2} mol/ L. The increase in the grafting parameters with monomer concentration might be due to the greater availability of monomer molecules in chain propa-

gating step. The retardation in grafting parameters might be attributed to the formation of poly (4-vinyl pyridine) along with graft copolymer, which increased the viscosity of the reaction medium.

Effect of sulfuric acid concentration

The variation of $[H^+]$ was studied by varying the concentration of sulfuric acid to the reaction mixture and the results are summarized in Table III. The variation of $[H^+]$ (2.5×10^{-3} to 15.0×10^{-3} mol/L) showed that grafting ratio, efficiency, add on and conversion were found to increase on increasing the $[H^+]$ up to 10×10^{-3} mol/L. This behavior can be explained with the help of the following equation:


On increasing the concentration of the hydrogen ion, AA$^\bullet$ species increases which reacts with peroxymonosulphate to give primary free radicals ($^\bullet$OH and AA$^\bullet$). These primary free radicals react with 4-vinyl pyridine and guar gum molecules giving macro guar gum and 4-vinyl pyridine radicals, which are responsible for the propagation of growing grafted chains. But on further increasing the concentration of hydrogen ion, i.e., beyond 10.0×10^{-2} mol/L, the total conversion and homopolymer were found to decrease, which might be due to premature termination of 4-vinyl pyridine radicals.

TABLE III
Effect of Sulphuric Acid Concentration on Grafting Parameters

$[H^+] \times 10^3$ mol/L	%G	%E	%A	%C	%H
2.5	212.2	44.8	78.7	27.4	55.2
5.0	380.1	46.0	79.2	38.4	54.0
10.0	521.0	47.4	83.8	51.1	52.6
15.0	350.0	42.3	77.8	42.0	57.7

[AA] = 4.0×10^{-3} mol/L, [4-vp] = 20.0×10^{-2} mol/L, $[HSO_5^-]$ = 10.0×10^{-4} mol/L, [GOH] = 1.0 g/L, time = 120 min, temperature = 35°C.
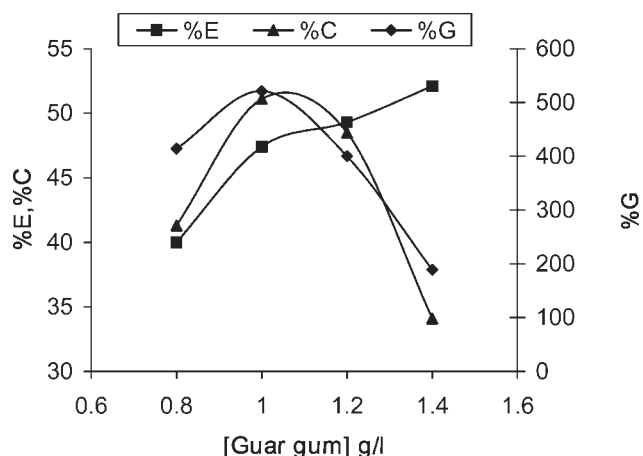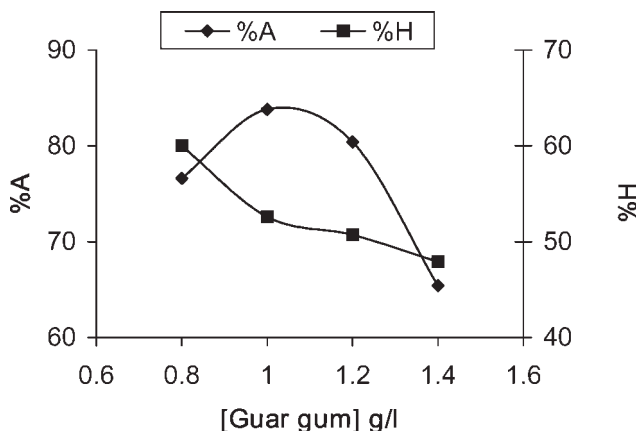
Figure 3 Effect of guar gum concentration $[HSO_5^-]$ = 10.0×10^{-4} mol/L; [AA] = 4.0×10^{-3} mol/L; $[H^+]$ = 10.0×10^{-3} mol/L [4-vp] = 20.0×10^{-2} mol/L; time = 120 min; temperature = 35°C.

Effect of guar gum concentration

The effect of guar gum was studied by changing the concentration from 0.8 to 1.4 g/L. As the concentration of guar gum was increased from 0.8 to 1.2 g/L (Figs. 3 and 4), the grafting ratio was increased. It might be due to the greater availability of the grafting sites at guar gum molecules. On further increasing the concentration of guar gum, the viscosity of the reaction medium increased, which hinders the movement of free radicals, thereby decreasing the grafting ratio.

Effect of time period

The effect of reaction time was studied by changing the time period of the reaction from 90 to 180 min. (Table IV). An increase in the grafting ratio, efficiency, add on, and conversion with increasing time period from 90 to 120 min was observed. Beyond

Figure 4 Effect of guar gum concentration $[HSO_5^-]$ = 10.0×10^{-4} mol/L; [AA] = 4.0×10^{-3} mol/L; $[H^+]$ = 10.0×10^{-3} mol/L; [4-vp] = 20.0×10^{-2} mol/L; time = 120 min; temperature = 35°C.

TABLE IV
Effect of Time on Grafting Parameters

Time (min)	%G	%E	%A	%C	%H
90	421.6	46.8	80.0	42.0	53.2
120	521.0	47.4	83.8	51.1	52.6
150	488.7	42.7	83.0	53.2	57.3
180	403.7	34.2	81.1	54.8	65.8

[AA] = 4.0×10^{-3} mol/L, [4-vp] = 20.0×10^{-2} mol/L, $[H^+]$ = 10.0×10^{-3} mol/L, [GOH]= 1.0 g/L, $[HSO_5^-]$ = 10.0×10^{-4} mol/L, temperature = 35°C.

this time period grafting ratio, efficiency and add on decreased, while conversion and homopolymer were found to increase. With increase in the time period up to 120 min. propagation of grafting chains takes place due to availability of more active species, which is responsible for higher grafting. On further increase in time period, the mutual annihilation of growing grafted chains occurred, which resulted in the decrease in grafting ratio, add on, efficiency, and increase in homopolymer formation.

Effect of temperature

The results obtained for grafting parameters at different temperatures are summarized in Table V. It is observed that as the temperature was increased from 30 to 35°C, grafting ratio, efficiency and add on increased, which might be due to production of more •OH and AA• free radicals causing an increase in these parameters. But on further increment in the temperature, the grafting parameters showed a decreasing trend because at higher temperature potassium peroxymonosulphate decomposed to give HSO_4^-, H_2O, and O_2 as reported by Cotton and Wilkinson.[13] Since O_2 acts as a scavenger for free radicals decreasing the concentration of all types of radicals, the grafting parameters decreased at higher temperature.

Mechanism

The following mechanism has been proposed for the graft copolymerization of 4-vinyl pyridine on to guar

TABLE V
Effect of Temperature on Grafting Parameters

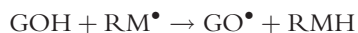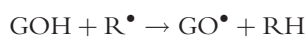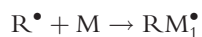| Temperature (°C)	%G	%E	%A	%C	%H
30	336.2	24.2	77.0	64.2	75.8
35	521.0	47.4	47.4	51.1	52.6
40	386.5	36.9	79.4	49.0	63.1
45	318.4	30.5	76.1	48.5	69.5

[AA] = 4.0×10^{-3} mol/L, [4-vp] = 20.0×10^{-2} mol/L, $[H^+]$ = 10.0×10^{-3} mol/L, [GOH] = 1.0 g/L, $[HSO_5^-]$ = 10.0×10^{-4} mol/L, time = 120 min.

gum using peroxymonosulphate/ascorbic acid redox pair.
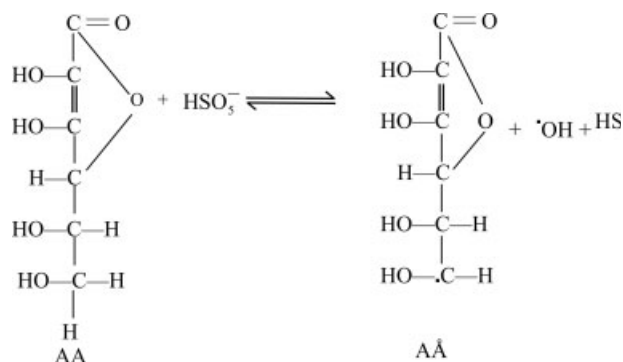
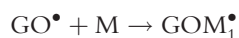$R^{\bullet}$ represents $AA^{\bullet}$ and $^{\bullet}OH$

Formation of free radicals

$$R^{\bullet} + M \rightarrow RM_1^{\bullet}$$

$$GOH + R^{\bullet} \rightarrow GO^{\bullet} + RH$$

$$GOH + RM^{\bullet} \rightarrow GO^{\bullet} + RMH$$

Initiation

$$GO^{\bullet} + M \rightarrow GOM_1^{\bullet}$$

Propagation

$$GOM_1^{\bullet} + M \rightarrow GOM_2^{\bullet}$$

$$GOM_2^{\bullet} + M \rightarrow GOM_3^{\bullet}$$

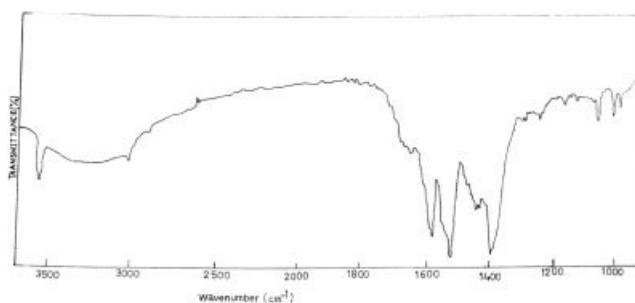$$\vdots \qquad \vdots \qquad \vdots$$
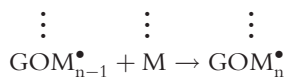
$$GOM_{n-1}^{\bullet} + M \rightarrow GOM_n^{\bullet}$$

Figure 5 IR spectra of guar gum.
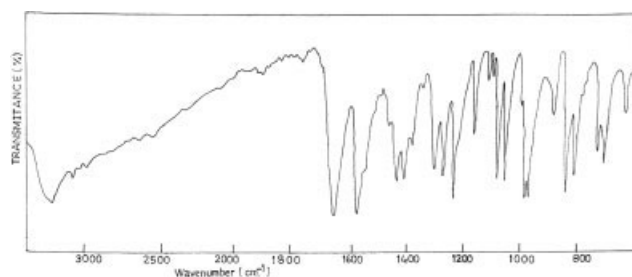
Figure 6 IR spectra of guar gum-*g*-4-vinyl pyridine.

$$RM_1^{\bullet} + M \rightarrow RM_2^{\bullet}$$

$$RM_2^{\bullet} + M \rightarrow RM_3^{\bullet}$$

$$\vdots \qquad \vdots \qquad \vdots$$

$$RM_{n-1}^{\bullet} + M \rightarrow RM_n^{\bullet}$$

Termination

$$GOM_m^{\bullet} + GOM_n^{\bullet} \rightarrow \text{graft copolymer (by coupling)}$$

$$GOM_n^{\bullet} + RM_n^{\bullet} \rightarrow \text{graft copolymer (by coupling)}$$

$$RM_n^{\bullet} + RM_m^{\bullet} \rightarrow \text{homopolymer (by coupling)}$$
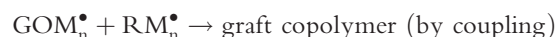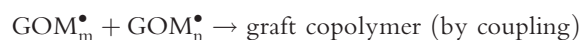
where AA is ascorbic acid, AA^{o} is ascorbic acid radical, and M is the monomer

Evidence of grafting

FTIR spectra

The FTIR spectra of solid sample of synthesized graft copolymer and ungrafted gum have been recorded on Perkin–Elmer FTIR spectrophotometer. On comparing the IR spectra of guar gum and guar gum-g-4-Vinyl pyridine the following additional bands in the spectrum of guar gum-g-4-vinyl pyridine are observed. Ring stretching vibration occurred
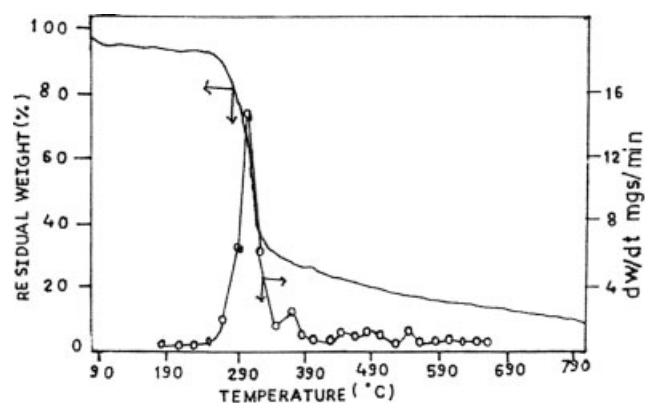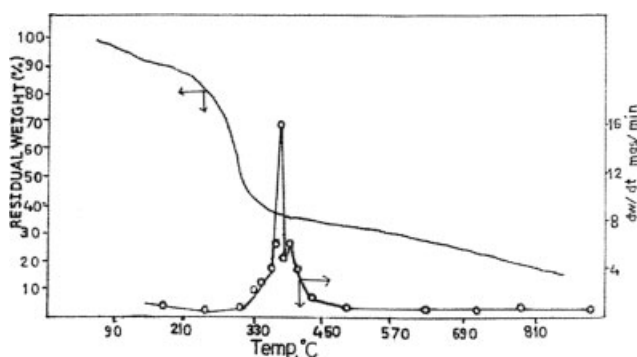

Figure 7 Thermogravimetric trace of guar gum.

Figure 8 Thermogravimetric trace of guar gum-*g*-4-vinyl pyridine.

in the region at 1665 and 1315 cm^{-1}, this absorption involves stretching of all the bonds in the pyridine ring(C = C, C = N). The band at 720 and 744 cm^{-1} are due to out of plane bending vibration of C-H in pyridine ring. The presence of these bands confirms the grafting of 4-Vinyl pyridine on to guar gum (Fig. 5 and 6).

Thermogravimetric analysis of guar gum-*g*-4-vinyl pyridine and guar gum

The thermogravemetric analysis of guar gum and its graft copolymer with 4-vinyl pyridine have been recorded on NETZSCH-Geratebau-GmbH thermal analyser in nitrogen atmosphere at the heating rate of 10°C/min.

Guar gum

Thermogravimetric analysis of guar gum reveals that decomposition of guar gum started at 230°C, and so it was a single step degradation process. The rate of weight loss increased on increasing the temperature up to 310°C, but thereafter, rate of weight loss is found to decrease. About 68% weight loss occurred between 200 and 400°C, and only 5% char yield was obtained at 800°C. The final decomposition temperature (FDT) was 320°C. The polymer decomposition temperature (PDT), T_{max} and integral procedural decomposition temperature (IPDT) of guar gum have been found at 280°C, 310°C, and 318.8°C, respectively (Fig. 7).

Guar gum-g-4-vinyl pyridine

Single step degradation is observed in guar gum-*g*-4-vinyl pyridine. The rate of weight loss increased on increasing the temperature from 300 to 360°C, but gradually decreased thereafter. The polymer decom-

position temperature (PDT) was 250°C and the temperature at which maximum degradation (T_{max}) occurred was 436°C. About 58% weight loss was observed between 210 and 350°C. This weight loss was lower than the weight loss in guar gum in the same temperature range. The integral procedural decomposition temperature (IPDT) and final decomposition temperature (FDT) have been found at 227.1°C and 570°C, respectively. At 850°C, 15% residual weight was obtained, which is more than the guar gum, indicating that synthesized graft copolymer is thermally more stable than guar gum (Fig. 8).

CONCLUSIONS

1. Guar gum grafted with 4-vinyl pyridine has been synthesized by employing an efficient redox system, i.e., peroxymonosulphate/ascorbic acid.
2. The spectroscopic data confirm that the grafting of 4-vinyl pyridine has occurred on guar gum.
3. The thermal analysis data showed that the synthesized graftcopolymer is more thermally stable than the ungrafted guar gum by considering the value of FDT and char yield.
4. The synthesized graftcopolymer can be used as a coating material when protection from excessive heat is needed.

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