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Graft copolymerization of acrylic acid onto guar gum initiated by vanadium (V)–mercaptosuccinic acid redox pair

Peeyoosh Kant Pandey, Arti Srivastava, Jasaswini Tripathy, Kunj Behari *

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

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Abstract

Guar gum has been modified by graft copolymerization with acrylic acid in aqueous medium using vanadium (V)–mercaptosuccinic acid redox system. The optimum reaction conditions affording maximum grafting ratio, efficiency, add on and conversion have been determined. The grafting parameters have been found to increase with increase in vanadium (V) concentration upto 1.0×10^{-2} mol dm^{-3}, but these parameters decrease on further increasing the vanadium (V) concentration. On increasing the mercaptosuccinic acid concentration from 1.0×10^{-2} to 4.0×10^{-2} mol dm^{-3} grafting ratio, efficiency and add on increase up to 2.0×10^{-2} mol dm^{-3} but decrease with further increase in mercaptosuccinic acid concentration. On varying the acrylic acid concentration from 5.0×10^{-2} to 30.0×10^{-2} mol dm^{-3}, maximum grafting ratio, efficiency and add on have been obtained at 20.0×10^{-2} mol dm^{-3}. The grafting ratio, add on and conversion increase, on increasing the H^+ ion concentration from 1.5×10^{-1} to 6.0×10^{-1} mol dm^{-3}. On increasing the guar gum concentration the grafting parameters increase. The grafting ratio, add on and conversion have been found to increase with time period while efficiency started decreasing after 120 min. It has been observed that $\%G$ increases on increasing the temperature up to 35 °C. The graft copolymer has been characterized by IR spectroscopy and thermogravimetric analysis.

Keywords: Guar gum; Acrylic acid; Graft copolymerization; Mercaptosuccinic acid; Vanadium

1. Introduction

Guar gum is a rigid, non-ionic, neutral carbohydrate polymer. It is one of the few carbohydrate natural polymers (Goldstein, Alter, & Seaman, 1973; Seaman, 1980) which has been used extensively in industry. Utilizing its properties, it has been used in industries such as mining (Atwood & Bourne, 1953), food (Werben, 1950), pharmaceuticals (Eartherton, Platz, & Crosgrove, 1955), and paper, etc. However, Whistler (Whistler, 1973) pointed out the drawback that guar gum suffers from biodegradibility, which limits its applications but this drawback can be improved through grafting of synthetic polymers. It have been reported that the grafting of polyacrylamide onto guar gum gives stability towards biodegradation (Deshmukh & Singh, 1987) and drag-reducing properties can also be enhanced (Deshmukh, Singh, & Chaturvedi, 1985). Acrylic acid, which is a vinyl monomer, possesses some unique characteristics and the polymers derived from it find many commercial applications (Greenwald & Luskin, 1980). Furthermore, grafting of acrylic acid onto different types of natural polymers is reported to have wide range of application in various fields (Chen, Kang, & Neoh, 2000; Hebeish, El-Zairy, El-Rafie, Higazy, & El-sisy, 1991; Pedram, Retuert, & Quijade, 2000). Therefore, an attempt has been made to synthesize guar gum-g-polyacrylic acid.

2. Experimental technique

2.1. Materials

Acrylic acid (E. Merck) was distilled in presence of copper turning under reduced pressure and only the middle

* Corresponding author.
E-mail address: reach2arti@yahoo.co.uk (K. Behari).

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fraction was used for grafting. Ammonium metavanadate (E. Merck), Mercaptosuccinic acid (Sigma) were used as such. Guar gum was obtained from Hindustan Gums and Chemicals Ltd. as a gift and used as such. Sulphuric acid (E. Merck) was used as source of hydrogen ions.

2.2. Procedure for graft copolymerization

Guar gum solutions were prepared by adding the desired amount to 100 ml triple distilled water in a reactor kept in a thermostat at the desired temperature. A definite amount of mercaptosuccinic acid, acrylic acid, and sulphuric acid solutions were added to the guar gum solution. The stream of nitrogen gas was passed to the solution in the reactor and vanadium (V) solution separately. After the desired time interval, the reaction was initiated by addition of a vanadium (V) solution of the desired concentration. The reaction was allowed to continue for the required time after which the reaction mixture was poured into methanol–water mixture (1:1.4 ratio). The graft copolymer precipitates out, where as polyacrylic acid, remains in the solution. The graft copolymer was separated by filtration and washed with methanol–water mixture two times, so that any homopolymer stuck to the graft copolymer sample passed into the filtrate. The graft copolymer thus obtained was dried and weighed. Polyacrylic acid was precipitated by acidifying the filtrate (Elayaperumal, Balkrishna, & Santappa, 1982) and it was filtered, dried and weighed.

3. Results and discussion

The graft copolymers were characterized according to Fanta's (1973) definition:

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

$$\text{Add on } (\%A) = \frac{\text{Weight of synthetic polymer}}{\text{Weight of graft copolymer}} \times 100,$$

$$\text{Conversion } (\%C) = \frac{\text{Weight of polymer formed}}{\text{Weight of monomer charged}} \times 100,$$

$$\text{Efficiency } (\%E) = \frac{\text{Weight of grafted polymer}}{\text{Weight of polymer formed}} \times 100,$$

$$\text{Homopolymer } (\%H) = 100 - \%E.$$

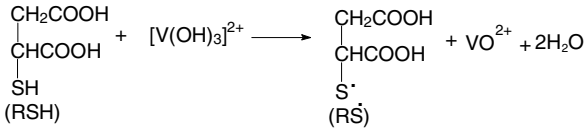
3.1. Effect of vanadium (V) concentration

The effect of vanadium (V) on the grafting parameters was studied by varying the concentration of vanadium ions from 5.0×10^{-3} to 25.0×10^{-3} mol dm^{-3}. The grafting ratio, efficiency, add on and conversion increased on increasing the concentration of vanadium (V) up to 10.0×10^{-3} mol dm^{-3} (Table 1) but decreased thereafter. The increment in the grafting parameters is due to increase in the production of primary free radicals, leading to an increase in the concentration of free radicals, which are responsible for grafting. However, at higher concentration of vanadium (V), oxidative termination of primary free radical leads to decrease in the grafting parameters (Eqs. (1) and (2)):

Table 1
Effect of vanadium (V) concentration

$[V(v)] \times 10^2$ mol dm^{-3}	%G	%E	%A	%C	%H
0.5	102.2	52.7	50.5	13.2	47.3
1.0	125.2	57.4	55.6	14.8	42.6
1.5	110.1	53.1	52.4	14.0	46.9
2.5	81.1	50.0	44.8	11.0	50.0

[Mercaptosuccinic acid] $= 2.0 \times 10^{-2}$ mol dm^{-3}, [acrylic acid] $= 2.0 \times 10^{-1}$ mol dm^{-3}, [guar gum] $= 9.78 \times 10^{-1}$ g dm^{-3}, [H^+] $= 3.0 \times 10^{-1}$ mol dm^{-3}, time = 120 min, temperature = 35 °C.



(1)

$$RS^{\cdot} + V^{5+} \rightarrow \text{Oxidation product} + V^{4+} \quad (2)$$

3.2. Effect of mercaptosuccinic acid

The grafting reactions were conducted by varying the mercaptosuccinic acid concentration from 1.0×10^{-2} to 4.0×10^{-2} mol dm^{-3} (Table 2). It was observed that grafting ratio, efficiency and add on increased as the concentration of mercaptosuccinic acid was increased from 1.0×10^{-2} to 2.0×10^{-2} mol dm^{-3}. On further increasing the concentration these parameters decreased. Initially with an increase in the mercaptosuccinic acid concentration primary free radicals are formed in greater numbers thereby increasing the grafting ratio, efficiency and add on but beyond the cited concentration of mercaptosuccinic acid, the formation of homopolymer increases as evident from the values, and this leads to decrease in the above grafting parameters.

3.3. Effect of acrylic acid

The acrylic acid concentration was varied from 5.0×10^{-2} to 30×10^{-2} mol dm^{-3} (Fig. 1) to study its effects on grafting parameters. The grafting ratio, efficiency and add on were found to increase on increasing the acrylic acid concentration upto 20.0×10^{-2} mol dm^{-3}, but beyond

Table 2
Effect of mercaptosuccinic acid concentration

$[MSA] \times 10^2$ mol dm^{-3}	%G	%E	%A	%C	%H
1.0	112.2	40.6	52.8	18.8	59.4
2.0	125.2	57.4	55.6	14.8	42.6
3.0	92.2	35.0	48.1	18.0	65.0
4.0	77.4	13.1	43.6	20.7	86.9

[V^{+5}] $= 1.0 \times 10^{-2}$ mol dm^{-3}, [acrylic acid] $= 2.0 \times 10^{-1}$ mol dm^{-3}, [H^+] $= 3.0 \times 10^{-1}$ mol dm^{-3}, [guar gum] $= 9.78 \times 10^{-1}$ g dm^{-3}, time = 120 min, temperature = 35 °C.

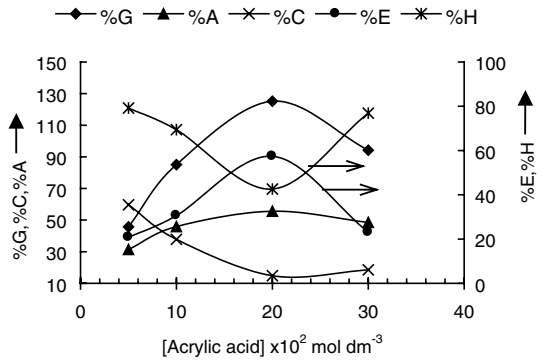


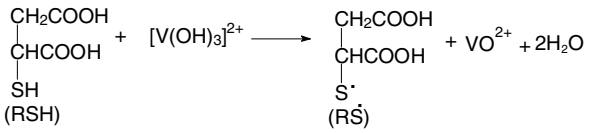
Fig. 1. Effect of acrylic acid concentration [mercaptosuccinic acid] = 2.0×10^{-2} mol dm^{-3}, [V^{+5}] = 1.0×10^{-2} mol dm^{-3}, [H^{+}] = 3.0×10^{-1} mol dm^{-3}, [guar gum] = 9.78×10^{-1} g dm^{-3}, time = 120 min, temperature = 35 °C.

this concentration these parameters decreased. The initial increase in grafting ratio, efficiency and add on is due to the greater availability of monomer molecules at the grafting sites, but beyond the cited concentration, due to the increase in polyacrylic acid concentration, the viscosity of the reaction medium increases. This restricts the movement of monomer molecules to the active sites on the backbone, thereby decreasing the grafting ratio, efficiency and add on.

3.4. Effect of hydrogen ions

Hydrogen ion concentration was varied from 1.5×10^{-1} to 6.0×10^{-1} mol dm^{-3} (Fig. 2). It was observed that grafting ratio, add on and conversion increased with the increase in hydrogen ion concentration. This observation is explained by the fact that in the aqueous medium vanadium (V) exists as VO_2^{+} and with increasing hydrogen ion concentration reacts with these ions to give $[V(OH)_3]^{2+}$, which is a better oxidant (Littler & Waters, 1959). The species $[V(OH)_3]^{2+}$ reacts with mercaptosuccinic acid producing primary free radical. Thus, with increasing hydrogen ion concentration production of primary free radical increases thereby increasing the grafting ratio, add on and conversion (Eqs. (3) and (4))

$$VO_2^{+} + H_3O^{+}[V(OH)_3]^{2+} \tag{3}$$



(4)

3.5. Effect of guar gum

The effect of guar gum on grafting reaction was studied by varying the gum concentration from 4.5×10^{-1} to 12.1×10^{-1} g dm^{-3} and the results are summarized in Table 3. The table reveals that grafting ratio, efficiency, add on and conversion increased with increase in the gum concentration. This increment may be due to the availability of more grafting sites, where polyacrylic acid can be grafted.

3.6. Effect of reaction time

The graft copolymerization was conducted for different time intervals from 90 to 180 min (Fig. 3) to study the effect of the duration of the reaction on grafting parameters. The grafting ratio, efficiency, add on and conversion increased with increase in duration of reaction. This increase in grafting parameters may be due to the more and more addition of monomer molecules to the growing grafted chain.

Table 3
Effect of guar gum concentration

[Guar gum] × 10^2 g dm^{-3}	%G	%E	%A	%C	%H
45.1	87.3	40.7	46.7	6.7	59.3
68.2	115.7	52.7	53.6	10.4	47.3
97.8	125.2	57.4	55.6	14.8	42.6
121.4	160.4	63.6	61.5	21.3	36.4

[V^{+5}] = 1.0×10^{-2} mol dm^{-3}, [mercaptosuccinic acid] = 2.0×10^{-1} mol dm^{-3}, [acrylic acid] = 2.0×10^{-1} mol dm^{-3}, [H^{+}] = 3.0×10^{-1} mol dm^{-3}, time = 120 min, temperature = 35 °C.

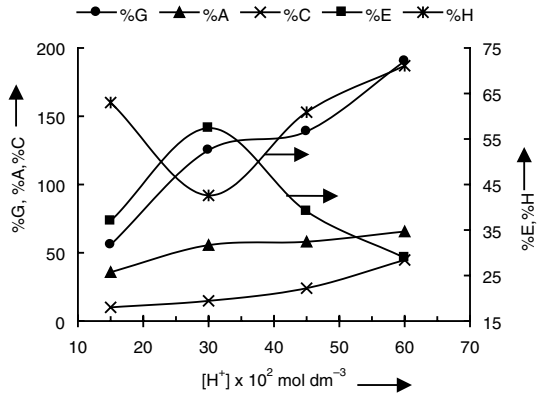


Fig. 2. Effect of hydrogen ion concentration [mercaptosuccinic acid] = 2.0×10^{-2} mol dm^{-3}, [V^{+5}] = 1.0×10^{-2} mol dm^{-3}, [acrylic acid] = 2.0×10^{-1}mol dm^{-3}, [guar gum] = 9.78×10^{-1} g dm^{-3}, time = 120 min, temperature = 35 °C.

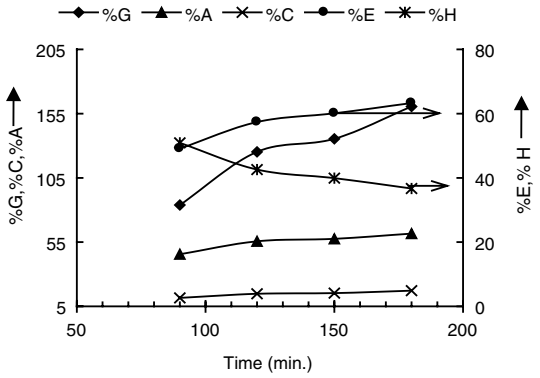


Fig. 3. Effect of time [V^{+5}] = 1.0×10^{-2} mol dm^{-3}, [mercaptosuccinic acid] = 2.0×10^{-2} mol dm^{-3}, [acrylic acid] = 2.0×10^{-1} mol dm^{-3}, [H^{+}] = 3.0×10^{-1} mol dm^{-3}, [guar gum] = 9.78×10^{-1} g dm^{-3}, temperature = 35 °C.

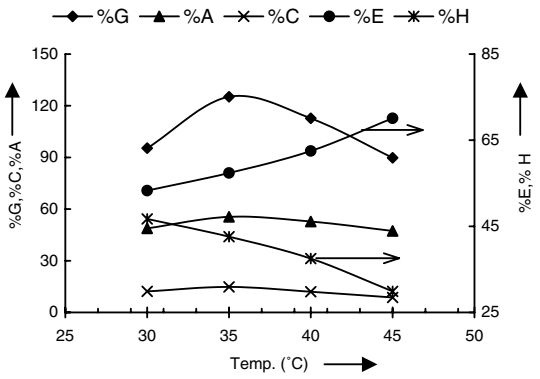


Fig. 4. Effect of temperature $[V^{+5}] = 1.0 \times 10^{-2}$ mol dm^3, [mercaptosuccinic acid] $= 2.0 \times 10^{-2}$ mol dm^{-3}, [acrylic acid] $= 2.0 \times 10^{-1}$ mol dm^{-3}, $[H^+] = 3.0 \times 10^{-1}$ mol dm^{-3}, [guar gum] $= 9.78 \times 10^{-1}$ g dm^{-3}, time = 120 min.

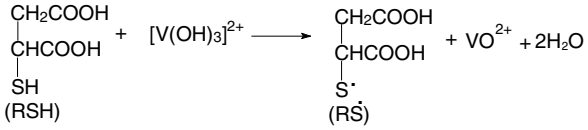
3.7. Effect of temperature

It was observed that grafting ratio, efficiency, add on and conversion increased on increasing the temperature from 30 to 35 °C (Fig. 4) but decreased with further increased in temperature while efficiency increases continuously. The increment in grafting parameters is attributed to the increase in the production of primary free radical with consequent increased in the number of grafting sites at polymer backbone, and increase in the rate of diffusion of acrylic acid onto the polymer backbone. The decrease in the grafting parameters is attributed to the premature termination of growing grafted chains at elevated temperature.

4. Mechanism

On the basis of experimental results following mechanism for grafting has been proposed:

The RS$^{\cdot}$ (primary free radical) is formed as follows:



(1)

The RS$^{\cdot}$ radical abstracts hydrogen atom from the guar gum molecule producing guar gum radical (GO$^{\cdot}$). The monomer molecules, which are in close vicinity of the reaction sites, become acceptor of guar gum radicals resulting in chain initiation and thereafter themselves become free radical donor to the neighbouring molecules leading to propagation. These grafted chains are terminated by coupling to give the graft copolymer.

Initiation:

$$RS^{\cdot} + GOH \rightarrow RSH + GO^{\cdot}$$

where GOH = guar gum

$$RS^{\cdot} + M \rightarrow RSM^{\cdot}$$

$$RSM^{\cdot} + GOH \rightarrow RSMH + GO^{\cdot}$$

Propagation:

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

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

$$- - - - - - - - - - - - - -$$

$$- - - - - - - - - - - - - -$$

$$GOM_{n-1}^{\cdot} + M \rightarrow GOM_n^{\cdot}$$

$$RSM^{\cdot} + M \rightarrow RSM_1^{\cdot}$$

$$RSM_1^{\cdot} + M \rightarrow RSM_2^{\cdot}$$

$$- - - - - - - - - - - - - -$$

$$- - - - - - - - - - - - - -$$

$$RSM_{n-1}^{\cdot} + M \rightarrow RSM_n^{\cdot}$$

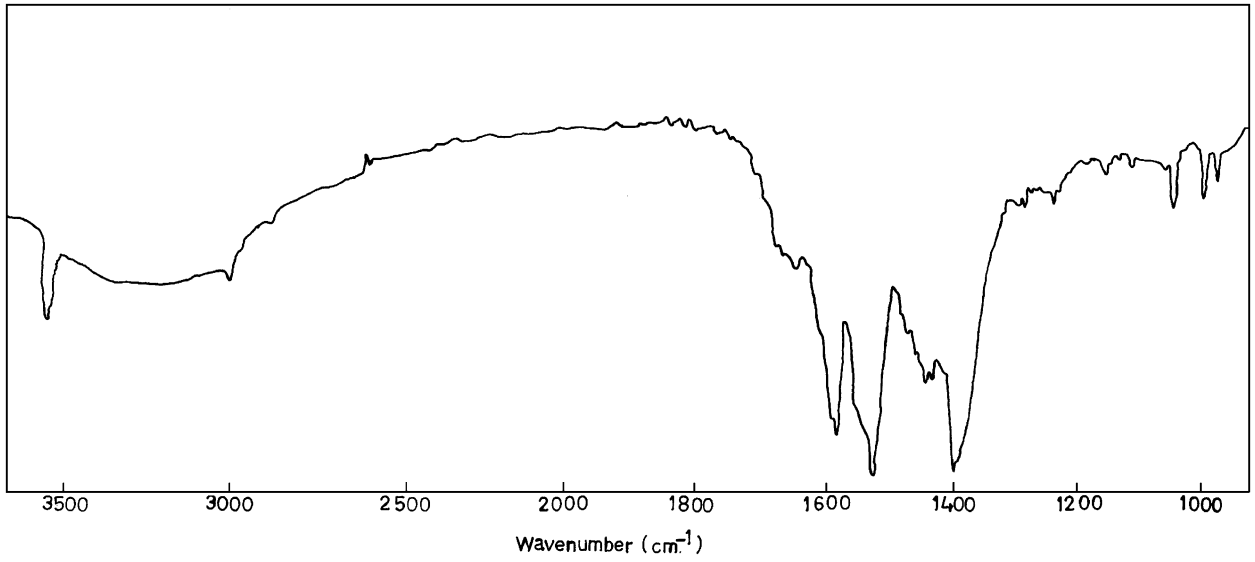


Fig. 5. IR spectra of guar gum.

Termination:

$$GOM_n^{\bullet} + GOM_m^{\bullet} \rightarrow \text{Graftcopolymer}$$
$$GOM_n^{\bullet} + RSM_m^{\bullet} \rightarrow \text{Graftcopolymer}$$
$$RSM_n^{\bullet} + RSM_m^{\bullet} \rightarrow \text{Homopolymer}$$

5. IR spectra

The FTIR spectra of guar gum and guar gum-g-acrylic acid have been recorded using the PERKIN ELMER–FTIR spectrophotometer PARAGON 1000 in the range 500–4000 cm^{-1}. On comparing the spectra of guar gum (Fig. 5) and guar gum-g-acrylic acid (Fig. 6) the following additional peaks/bands in the spectrum of guar gum-g-acrylic acid have been observed.

(i) The broad and intense band in the region 2730–3050 cm^{-1} is attributed to stretching vibration of O–H bond.
(ii) The peak at 1740 cm^{-1} is attributed to stretching vibration of carbonyl group of acrylic acid.
(iii) The broad and intense bands centered at 1240 and 1450 cm^{-1} are attributed to C–O stretching and C–O–H bending vibrations.

The presence of these bands/peaks confirms the grafting of poly acrylic acid onto the guar gum backbone.

Table 4
Thermogravimetric analyses of polymers

Sample	PDT (°C)	FDT (°C)	T_{max} (°C)	IPDT (°C)
Guar gum	260	320	310	318.8
Guar gum-g-polyacrylic acid	160	460	390	207.0

Fig. 6. IR spectra of guar gum-g-acrylic acid.

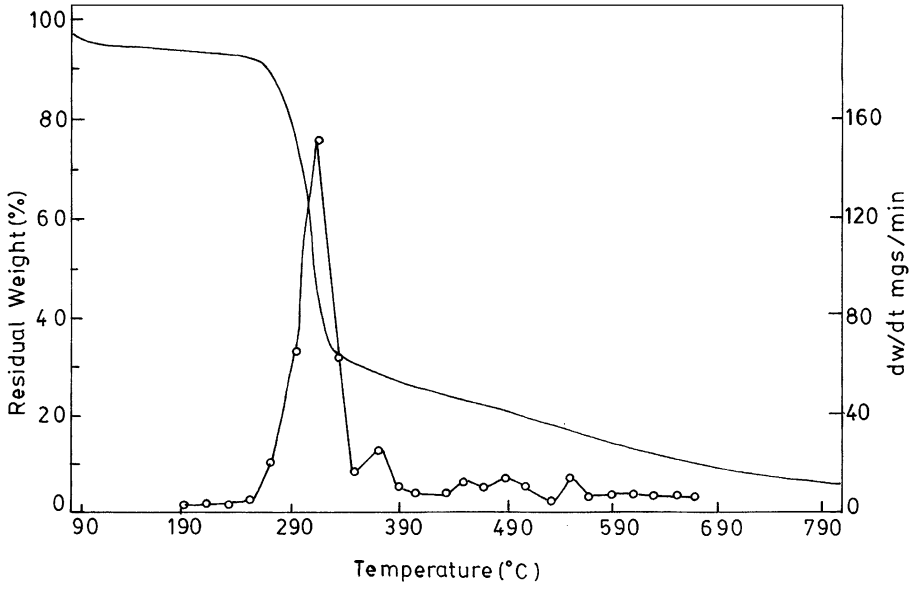


Fig. 7. Thermogravimetric trace of guar gum.

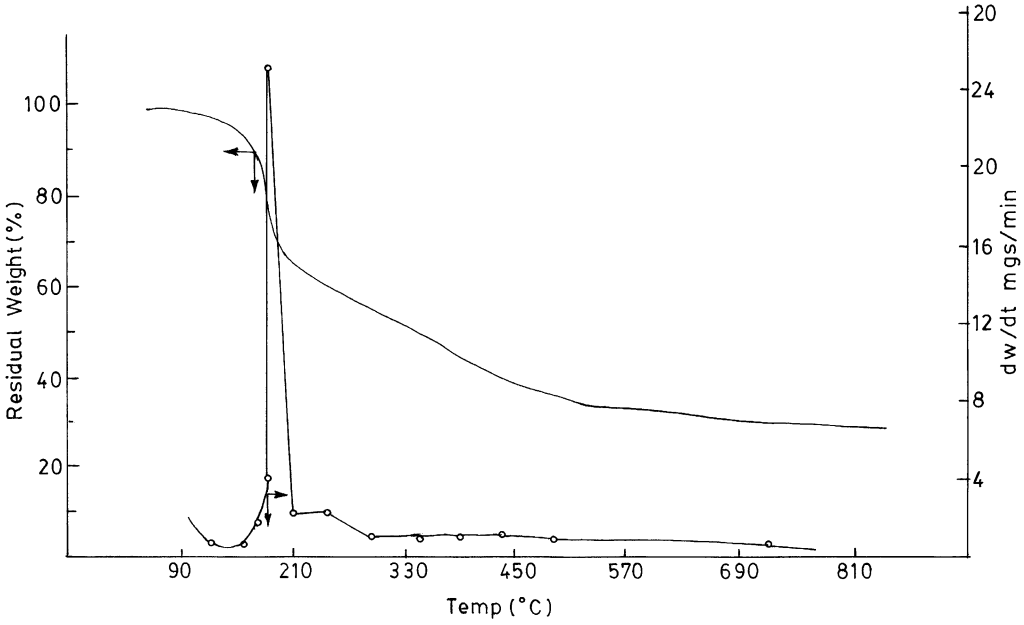


Fig. 8. Thermogravimetric trace of guar gum-g-acrylic acid.

6. Thermogravimetric analysis

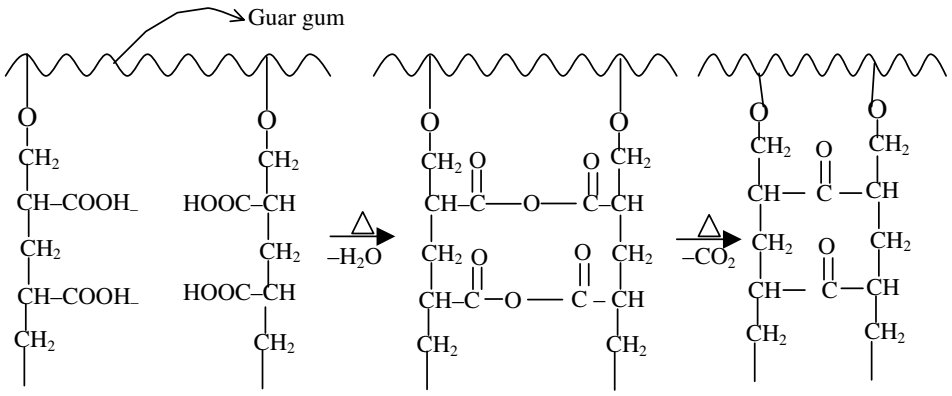
The thermogravimetric analysis of guar gum and its graft copolymer with acrylic acid have been recorded on NETZSCH-Geratebau GmbH thermal analyzer in nitrogen atmosphere at heating rate of 10 °C/min.

6.1. Guar gum

The decomposition of guar gum starts at 230 °C, this is single step degradation process (Fig. 7). The rate of weight loss increased upon increasing the temperature up to 310 °C, but thereafter it decreased. Nearly 75% of guar gum degrades below 400 °C. Therefore the final decomposition temperature (FDT) was very low, i.e., 320 °C. Temperature at which maximum degradation occur (T_{max}), polymer decomposition temperature (PDT), and integral procedural decomposition temperature (IPDT) of guar gum were found to be 310, 260, and 318.8 °C, respectively (Table 4). Only a 5% char yield was obtained at 800 °C.

6.2. Guar gum-g-acrylic acid

The graft copolymer began to degrade at about 150 °C (Fig. 8) and this is single step degradation process. About 4.5% weight loss was observed below this temperature due to absorbed water. The rate of weight loss increased with increase in temperature up to 210 °C and gradually decreased thereafter. The polymer decomposition temperature (PDT), temperature at which maximum degradation occur (T_{max}), final decomposition temperature (FDT) and integral procedural decomposition temperature (IPDT) were found to be 160, 390, 460 and 207 °C, respectively. Beyond 40% weight loss, rate of weight loss decreased with increase in temperature, therefore, T_{max} and FDT were higher than that of guar gum. The polymer decomposition temperature indicated that grafting of acrylic acid lowers the initial decomposition temperature because of the formation of anhydride with the elimination of water from the two neighbouring carboxylic groups of the grafted chains as shown in the following steps. About 68% weight loss occurred between 200 and 400 °C and 30% char yield was obtained at 800 °C.



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