One pot synthesis and characterization of industrially important graft copolymer (GOH-g-ACM) by using peroxymonosulphate/ mercaptosuccinic acid redox pair

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Abstract: Guar gum-g-polyacrylamide is a graft copolymer which is used for many industrial applications. This paper outlines the details of synthesis of guar gum -g-acrylamide by using potassium peroxymonosulphate/ mercaptosuccinic acid redox pair in an inert atmosphere and their characterization by infrared spectroscopy, UV analysis and study of swelling and thermal properties. Grafting characteristics: %G, %E, %C, %A and %H were determined by using Fanta's definition; rate of grafting was also calculated. On studying the effect of reaction conditions on grafting characteristics, it was found that the optimum concentration of peroxymonosulphate, mercaptosuccinic acid, hydrogen ion, acrylamide and guar gum for maximum % of grafting were 8.0×10^{-3}, 3.2×10^{-3}, 8.0×10^{-3}, 16.0×10^{-2} mol dm^{-3} and 60.0×10^{-2} g dm^{-3} respectively. The optimum time duration and temperature of reaction were found to be 120 min and 40 °C respectively. During the study $[H^{+}]$ variation showed prompt changes on grafting characteristics. It was found that after 310 °C the polyacrylamide grafted guar gum was thermally more stable than pure guar gum.

Introduction

Guar gum is a rigid, non ionic, neutral kind of plant glue. It is an edible carbohydrate polymer found in the seed of *Cynaposis tetragonolbus*. This polysaccharide is formed by galactose and mannose molecules. The principle backbone is a chain of (1→4)-ß-linked D-mannopyranosyl units linked to the main chain. There are between 1.5-2 mannose residues for every galactose residue (Fig. 1).
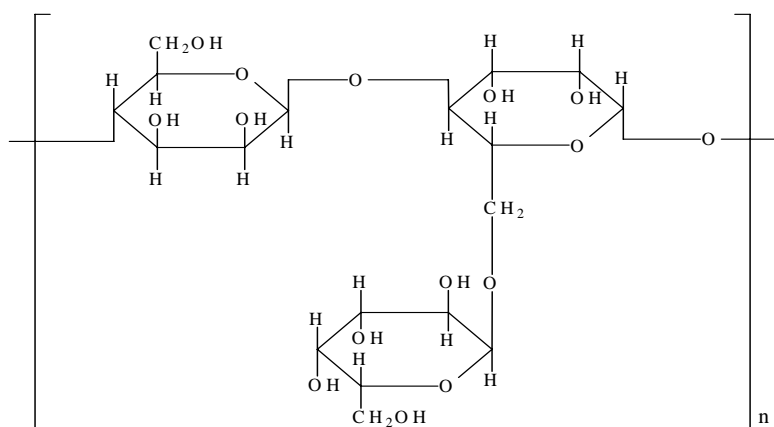

Fig. 1. Structure of Guar Gum.

The modification of guar gum by grafting of water-soluble vinyl monomers, results in the retention of desirable properties and incorporation of favorable functionalities. Such grafted gum has been used in the preparation of flocculants [1] and as a biodegradable drag reducing agent for industrial requirements [2].

Polyacrylamide has wide range of application in industries from paper manufacturing [3] and water treatment [4] through oil recovery [5] to soil modification [6] and medical applications [7]. Furthermore, the graft copolymers of acrylamide on different types of cellulose [8] revealed that various properties *viz* flocculation, solubility, thermal stability, binding strength, water retention and drag reduction effectiveness of the substrate increases. Besides these applications poly(acrylamide) has other multiple applications *viz* as polymer gel dosimeter [9], for water retention: owing to its high swelling capacity [10], in electrophoresis for separation of protein and DNA samples, as a model for drug delivery systems: for studying controlled drug release profiles [11-13].

In the past decade, a lot of studies were done on guar gum-g-polyacrylamide but in the synthesis of a graft copolymer the challenging problem is the formation of polyacrylamide homopolymer. Because of that we have searched a new redox pair which has yielded better % grafting over homopolymer, during this synthesis of graft copolymer several redox pairs were applied and only a peroxymonosulphate (PMS)/ mercaptosuccinic acid (MSA) redox pair gave the minimum amount of homopolymer. This uniqueness prompted us to hybridize the natural polymer with synthetic monomer which is of great interest due to its application as biomedical and biodegradable materials. This chemical combination of natural and synthetic monomers yielded a new material, which could have desirable properties including improved biodegradability and thermal stability.

Results and discussion

To determine the optimum condition for the grafting of acrylamide onto guar gum, using PMS/ mercaptosuccinic acid as redox initiator, graft copolymerization was carried out under various reaction time, temperature and concentrations of PMS, mercaptosuccinic acid, guar gum, hydrogen ion and acrylamide.

Influence of variables on grafting characteristics

-Effect of Peroxymonosulphate Concentration

The concentration of peroxymonosulphate was varied from 4.0 to 12.0 $\times 10^{-3}$ mol dm^{-3} for studying its effect on grafting ratio, grafting efficiency, add on, conversion, homopolymer and rate of grafting and the results are summarized in Tab. 1. It was observed that the grafting characteristics of acrylamide on guar gum increased with increasing the concentration of peroxymonosulphate. The increment in grafting characteristics was due to the progressive reduction of peroxymonosulphate by mercaptosuccinic acid producing large number of free radicals thereby enhancing all the grafting characteristics except homopolymer.

-Effect of Mercaptosuccinic acid Concentration

The effect of mercaptosuccinic acid on grafting characteristics was studied by varying the concentration of mercaptosuccinic acid from 2.4 to 4.0 $\times 10^{-3}$ mol dm^{-3}. From Tab. 2, it was observed that all the grafting characteristics increased on increasing the concentration of mercaptosuccinic acid up to 3.2 $\times 10^{-3}$ mol dm^{-3} except homopolymer, which showed the opposite trend after that it decreased.

Tab. 1. Effect of Potassium Peroxymonosulphate Concentration.

$[PMS] \times 10^3$ mol dm^{-3}	%G	%E	%C	%A	%H	Rg × 10^6 mol l^{-1} s^{-1}
4.0	108.0	45.4	20.9	51.9	54.6	27
6.0	120.0	51.3	20.6	54.5	48.7	30
8.0	135.0	55.5	21.4	57.4	44.4	34
10.0	180.0	62.71	25.2	64.2	37.2	45
12.0	198.0	65.6	26.6	65.5	34.4	50

[MSA] = 3.2×10^{-3} mol dm^{-3}; [ACM] = 16.0×10^{-2} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Time = 120 min.; Temp.= 40 °C.

The increment in %G, %E, %A, %C and Rg might be due to the increase in number of free radicals and decrement in grafting characteristics might be due to formation of homopolymer than graft copolymer and it is also supported by more formation of homopolymer.

Tab. 2. Effect of Mercaptosuccinic Acid Concentration.

$[MSA] \times 10^3$ mol dm^{-3}	%G	%E	%C	%A	%H	Rg × 10^6 mol l^{-1} s^{-1}
2.4	175.0	61.8	24.9	63.3	38.2	44
2.8	189.0	64.2	25.8	65.4	35.7	48
3.2	198.0	65.6	26.6	65.6	34.4	50
3.6	135.0	54.6	21.7	54.6	45.4	34
4.0	100.0	45.9	19.2	50.0	54.1	25

[PMS] = 12.0×10^{-3} mol dm^{-3}; [ACM] = 16.0×10^{-2} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Time = 120 min.; Temp. = 40 °C.

-Effect of Acrylamide Concentration

The effect of acrylamide on grafting characteristics was studied by varying the concentration of acrylamide from 8.0 to 22.0 ×10^{-2} mol dm^{-3} and results are shown in Fig. 2. It is observed that on varying the concentration of acrylamide from 8.0 to 22.0 ×10^{-2} mol dm^{-3} %G, %E, %A and Rg increased up to 16.0 × 10^{-2} mol dm^{-3} but %H decreased and beyond this concentration of acrylamide %G, %E ,%A and Rg were found to decrease. However, conversion increased continuously as the concentration of acrylamide increases. The increment in %G, %E, %A and Rg might be due to greater availability of acrylamide at the close proximity of the polymer backbone. The monomer molecule at the close proximity of the reaction site becomes acceptor of the guar gum radicals resulting in chain initiation. Thereafter, monomer molecule became free radical donor to the neighbouring molecules, in this way grafted chains grow. The decrease in %G, %E, %A and Rg could be explained in terms of increase in the viscosity of the reaction medium due to preferential formation of polyacrylamide at higher concentration of monomer.
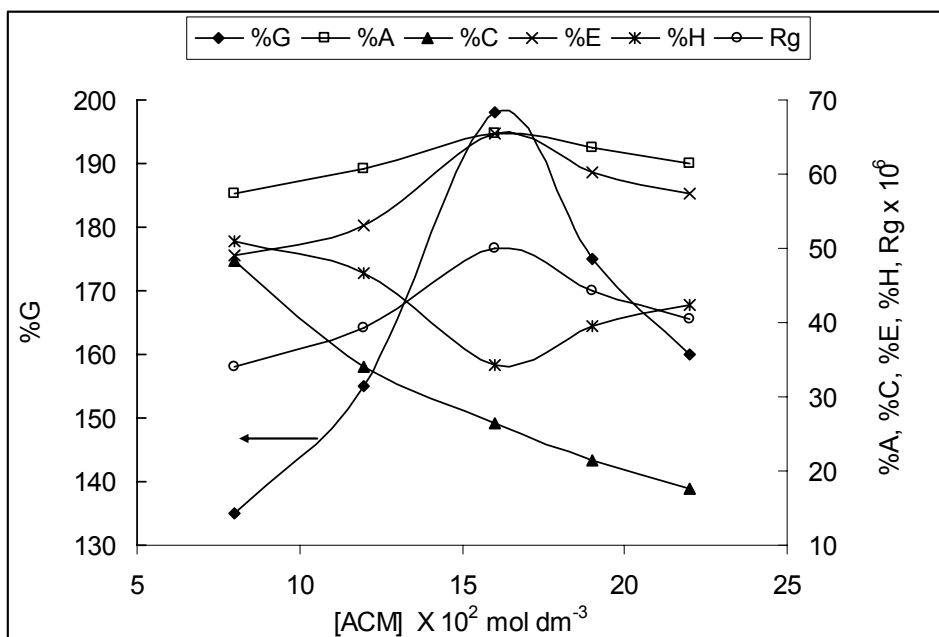
Fig. 2. Effect of acrylamide concentration. [PMS] = 12.0×10^{-3} mol dm^{-3}; [MSA] = 3.2×10^{-3} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Time = 120 min.; Temp. = 40°C, %G = Grafting ratio; %A = Add on; %C = Conversion; %E = Efficiency; %H = Homopolymer; Rg = Rate of grafting

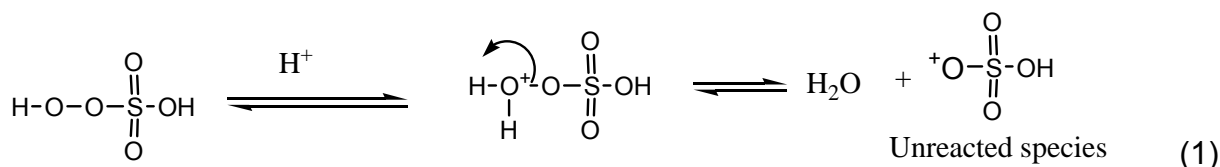-Effect of Hydrogen Ion Concentration

The graft copolymerization was carried out at different concentration of hydrogen ion (Tab. 3). It was observed that on increasing the hydrogen ion concentration from 8.0 to 16.0×10^{-3} mol dm^{-3} %G, %C, %E, %A and Rg decreased continuously. Thus from the result it can be concluded that hydrogen ion plays an important role with this redox pair in terms of grafting characteristics.

Tab. 3. Effect of Hydrogen ion Concentration.

[H$^+$] × 10^3 mol dm^{-3}	%G	%E	%C	%A	%H	Rg × 10^6 mol l^{-1} s^{-1}
8.0	225	69.0	28.7	69.2	31.0	56
10.0	208	66.9	27.4	67.5	33.1	52
12.0	198	65.5	26.6	65.6	34.4	50
14.0	160	60.0	23.4	61.5	40.0	40
16.0	120	51.5	20.5	54.5	48.5	30

[PMS] = 12.0×10^{-3} mol dm^{-3}; [MSA] = 3.2×10^{-3} mol dm^{-3}; [ACM] = 16.0×10^{-2} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Time = 120 min.; Temp.= 40 °C.

The decrement in grafting characteristics can be explained on the basis of fact that in the acidic medium peroxymonosulphate protonated to produce protonated species H$_3$SO$_5^+$ with increasing hydrogen ion concentration (eq. 1). Thus on increasing the hydrogen ion concentration, formation of protonated species took place due to which quantum of primary free radical decreased thereby %G, %E, %A, %C, Rg decreased and homopolymer increased.

$$H-O-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH \quad \xrightleftharpoons{H^+} \quad H-\overset{H}{\overset{|}{O^+}}-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH \quad \rightleftharpoons \quad H_2O \; + \; {}^+O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH$$

Unreacted species (1)

-Effect of Guar gum Concentration

From the Fig. 3 it is clear that %G, %E, %A and Rg decreased on increasing the concentration of guar gum from 60 to 220 ×10^{-2} mol dm^{-3}, while conversion and homopolymer increased. This behavior can be explained on the ground that viscosity of the reaction medium increases on increasing the guar gum concentration which hinders the movement of free radicals, therefore, decrement in the grafting ratio, efficiency, add on and rate of grafting were observed.
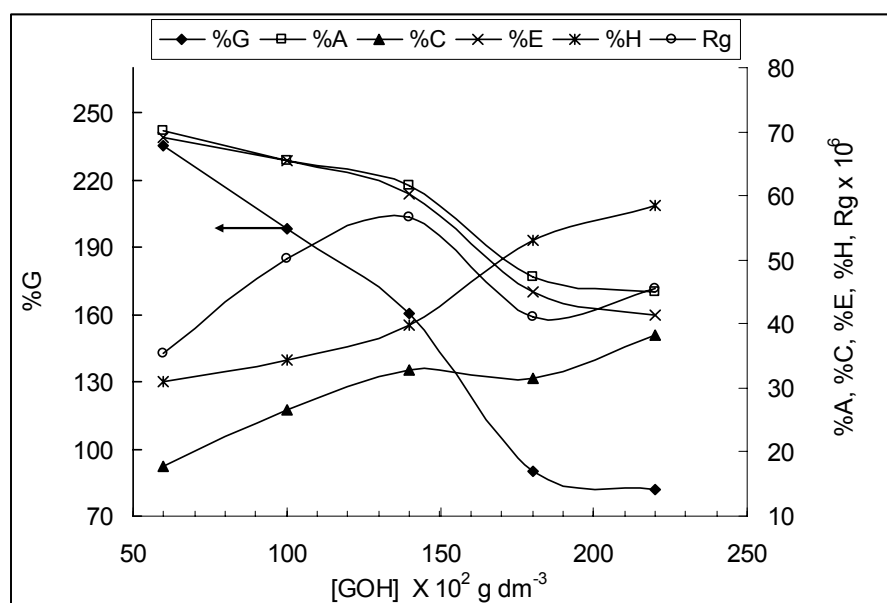

Fig. 3. Effect of Guar gum concentration. [PMS] = 12.0×10^{-3} mol dm^{-3}; [MSA] = 3.2×10^{-3} mol dm^{-3}; [ACM] = 16.0×10^{-2} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; Time = 120 min.; Temp. = 40 °C; %G = Grafting ratio; %A = Add on; %C = Conversion; %E = Efficiency; %H = Homopolymer; Rg = Rate of grafting

-Effect of Time

The graft copolymerization reaction was conducted on intervals of time *i.e.* from 60 to 180 minutes for studying the effect of the duration of the reaction on grafting characteristics and rate of grafting (Fig. 4). It was observed that the grafting ratio, add on, efficiency and rate of grafting increased but homopolymer decreased as the time period of the reaction increases up to 120 minutes, while conversion increases upto 90 minute. The increase in grafting characteristics might be due to increasing concentration, subsequent additions of monomer molecules to the growing grafted chains. But on further increasing time period grafting ratio, add on, efficiency, rate of grafting were decreased and homopolymer increased. This behaviour can be explained that, all the active sites have been exhausted after 120 min. and beyond this time period the mutual annihilation of the growing grafted chains occurred, which resulted in the formation of homopolymer.
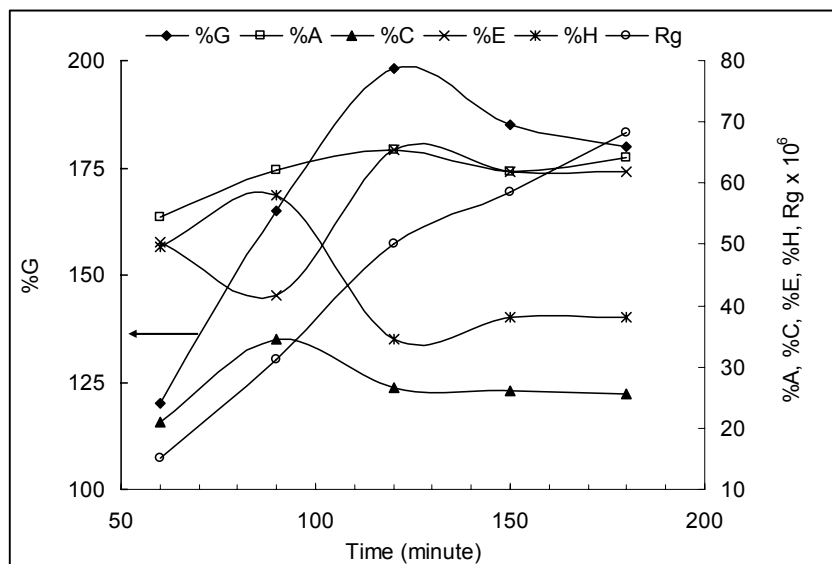
Fig. 4. Effect of Time. [PMS] = 12.0×10^{-3} mol dm^{-3}; [MSA] = 3.2×10^{-3} mol dm^{-3}; [ACM] = 16.0×10^{-2} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Temp = 40°C %G = Grafting ratio; %A = Add on; %C = Conversion; %E = Efficiency; %H = Homopolymer; Rg = Rate of grafting

-Effect of Temperature

The grafting reaction was carried out at various temperatures ranging from 30 °C to 50 °C (Fig. 5). On increasing the temperature grafting ratio, add on, conversion, efficiency and rate of grafting were found to increase but homopolymer decrease. This effect may be due to (I) the rate of production of primary free radicals increased, (II) the rate of diffusion of acrylamide onto guar gum matrix increased on increasing temperature. Similar effect was observed by Samal et. al. in the grafting of acrylamide on to Nylon-6 [14] and Silk fibers [15].
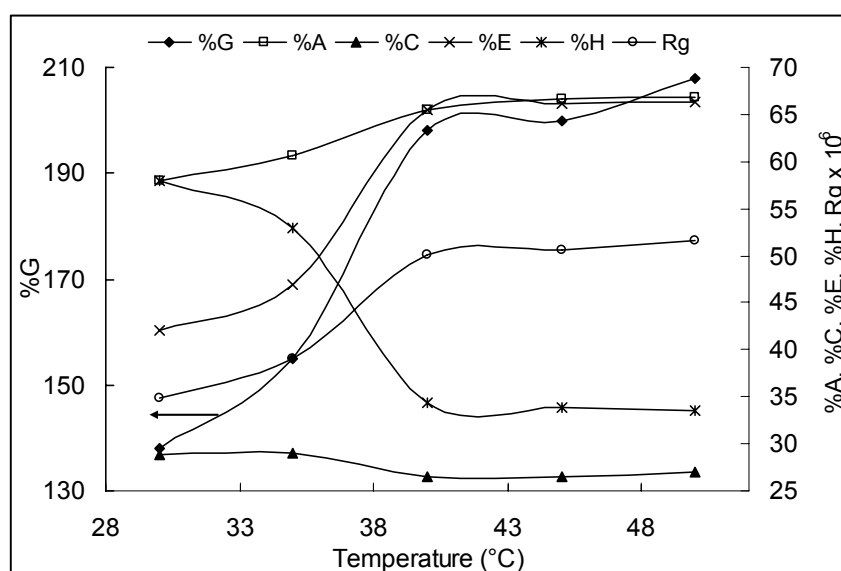

Fig. 5. Effect of Temperature.[PMS] = 12.0×10^{-3} mol dm^{-3}; [MSA] = 3.2×10^{-3} mol dm^{-3}; [ACM] = 16.0×10^{-2} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Time = 120 min. %G = Grafting ratio; %A = Add on; %C = Conversion; %E = Efficiency; %H = Homopolymer; Rg = Rate of grafting.

Swelling studies

It was observed that percent swelling and swelling ratio of graft copolymer increase on increasing the percent grafting ratio up to certain limits. This behaviour can be explained by fact that acrylamide is hydrophilic in nature and with increase in percent grafting the percentage of polyacrylamide also increases thereby increase in percent swelling and swelling ratio was observed.

Tab. 4. Swelling studies.

Sample code	$[ACM]\times10^2$ mol dm^{-3}	%G	P_S	S_R
GAm$_1$	8.0	135	312	3.12
GAm$_2$	12.0	155	390	3.90
GAm$_3$	16.0	198	480	4.80
GAm$_4$	19.0	175	420	4.20
GAm$_5$	22.0	160	389	3.89

[PMS] = 12.0×10^{-3} mol dm^{-3}; [MSA] = 3.2×10^{-3} mol dm^{-3}; [H$^+$] = 12.0×10^{-3} mol dm^{-3}; [GOH] = 1.0 g dm^{-3}; Time = 120 min.; Temp= 40 °C.

Evidence of grafting

-FTIR spectral analysis

The FTIR spectrum of guar gum-g-acrylamide (——) showed the characteristics peaks of polyacrylamide as well as guar gum (Fig. 6). Bands at 1650 cm^{-1} and 1560 cm^{-1} are attributed to C=O stretching and N-H bending vibration of polyacrylamide respectively.
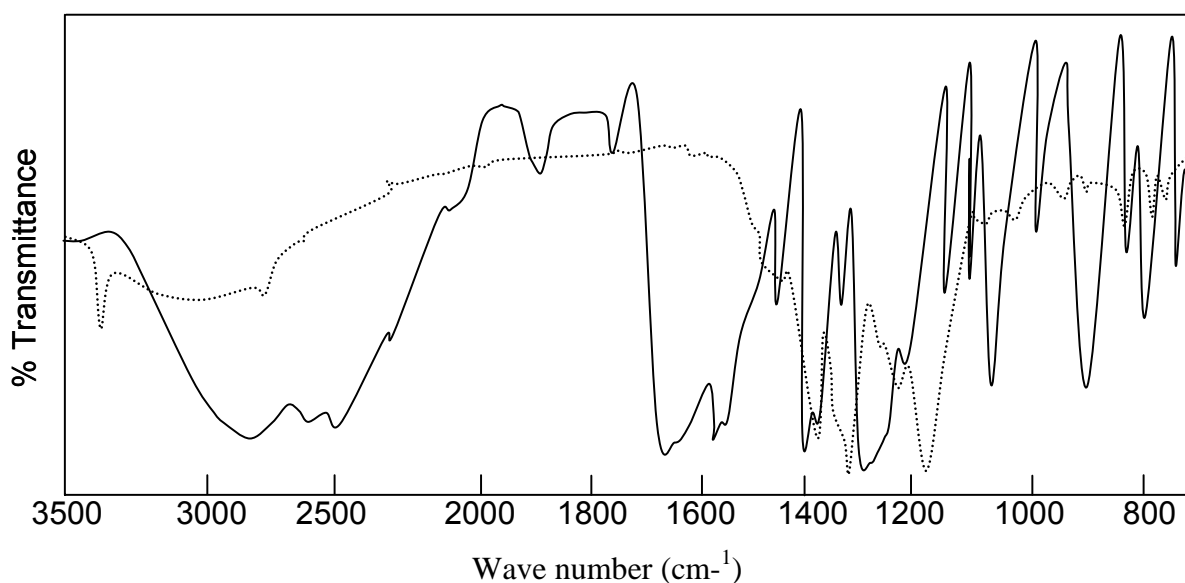

Fig. 6. IR spectrum of Guar gum (…..) and Guar gum-g-acrylamide (——).

The absorption involved coupling between N-H bending and other vibrations. Out of plane N–H wagging is responsible for a broad band of medium intensity in the range of 800-772 cm⁻¹. Amide II band in the region of 1575-1480 cm⁻¹ resulted from an interaction between the N-H bending and C-N stretching of the C-N-H group. The band near 1230 cm⁻¹ resulted from an interaction between the N-H bending and C-N stretching. Thus the presence of these bands and disappearance of O–H bending vibration in the spectrum of grafted gum proves that acrylamide was grafted on to O–H site of the guar gum macromolecule.

-UV Analysis

Fig. 7 shows UV visible spectra of guar gum (C), acrylamide (B) and guar gum-g-acrylamide (A) in the region 200 to 600 nm. UV-visible spectrum of guar gum shows no peak on 250 nm, while a broad peak was observed in acrylamide spectrum on 250 nm. The spectrum of guar gum-g-acrylamide clearly indicates the incorporation of above peak in the graft copolymer. This peak is due to carbonyl chromophore of amido group of acrylamide, which confirms the grafting of acrylamide onto guar gum.
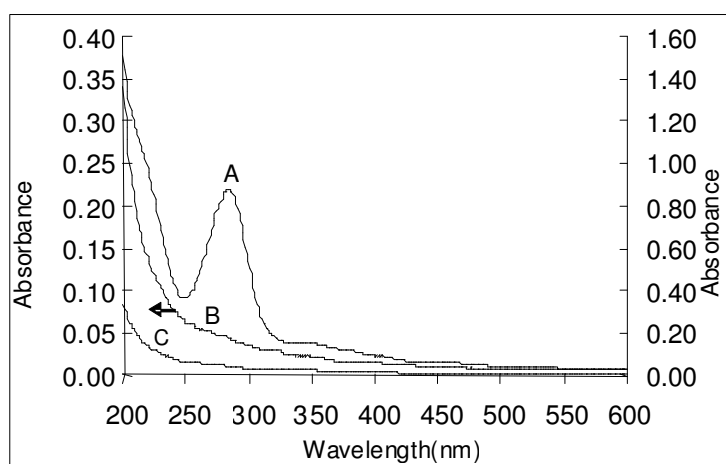

Fig. 7. UV-Visible Spectra of Grafted gum (A), Acrylamide (B), and Guar gum (C)

Thermal analysis

-Guar gum

Fig. 8 presents the thermo gram of guar gum (- - -) which reveals that decomposition of guar gum started at 230 ℃ and it is a single step degradation process. The rate of weight loss increased on increasing temperature up to 310 ℃, thereafter, rate of weight loss was found to decrease. About 68% weight loss occurred between 200 to 400 ℃ and 5% char yield was obtained at 800 ℃. Nearly 75% of guar gum degraded at 400 ℃ (Tab. 6). Therefore, the final decomposition temperature (FDT) occurred at very low temperature *i.e.* 320 ℃. The polymer decomposition temperature (PDT), T_{max} (temperature at which maximum degradation occurred) and integral procedural decomposition temperature (IPDT) of guar gum were found to be 260 ℃, 310 ℃ and 318.8 ℃ respectively (Tab. 5).

-Guar gum-g-acrylamide

Guar gum-g-acrylamide (—) starts to degrade at about 190 ℃, however, 4% weight loss was observed around 100 ℃ which is due to the absorbed water. The rate of weight loss increased on increasing the temperature from 150 ℃ to 400 ℃, but after

that it decreased slowly (Fig. 8). About 54% weight loss was observed at 500 °C (Tab.7), while 50% weight loss in case of guar gum was observed at 306 °C and a char yield of 15% was obtained at 800 °C.
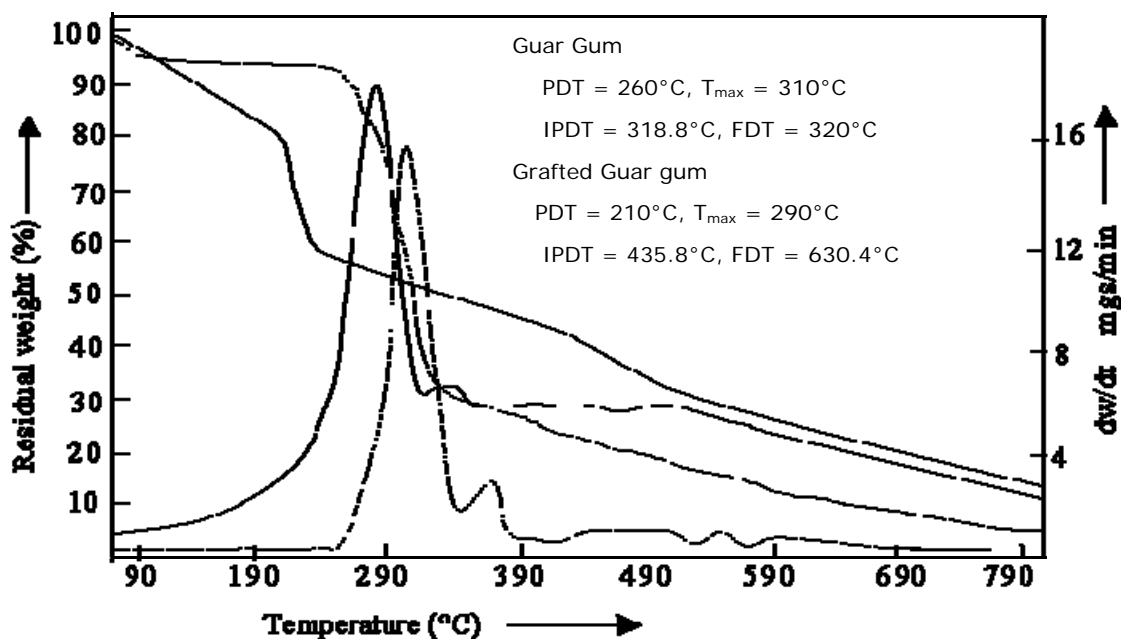

Fig. 8. Thermo gravimetric and Differential Thermogravimetric trace of Guar gum (- -) and Guar gum-g-Acrylamide (——).

The maximum weight loss (T_{max}) appeared at 290 °C and PDT, FDT, IPDT of guar gum-g-acrylamide were found to be 210 °C, 630.4 °C and 435.8 °C respectively (Tab. 5). The PDT and FDT indicated that grafting of acrylamide decreased the initial decomposition temperature by 50 °C while it increased the final decomposition temperature by 310 °C than that of guar gum. The grafting of acrylamide lowers the initial decomposition temperature of graft copolymers; polyacrylamide degraded [16] in the temperature range of 175-300°C by the formation of imide group via cyclization of imide group and evolution of ammonia (Fig. 9). This cyclized structure imparts further stability to guar gum molecule. The higher value of FDT, IPDT and char yield of grafted guar gum compared to those of guar gum indicates an overall improvement in thermal stability of the graft copolymer.
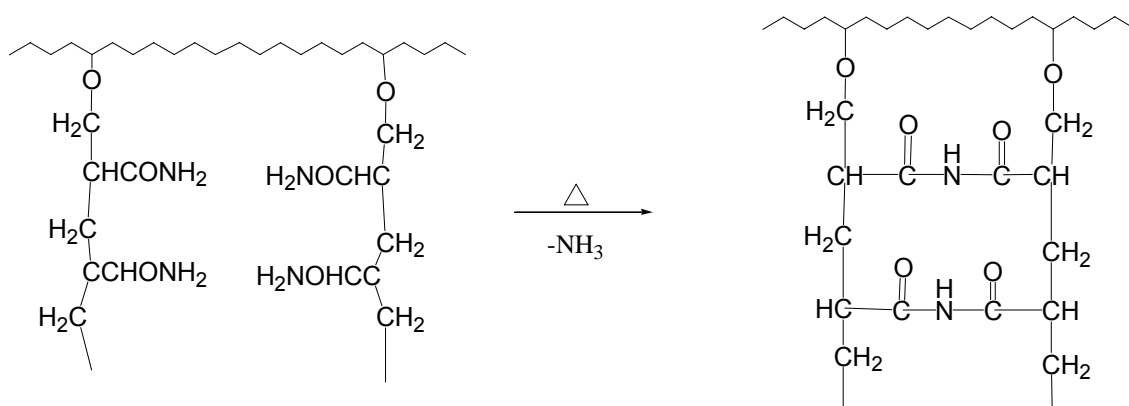

Fig. 9. Schematic decomposition of Guar gum-g-acrylamide.

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Tab. 5. Thermogravimetric Analyses of Ungrafted and Grafted Gum.

Sample Code	PDT(°C)	FDT (°C)	T_{max}(°C)	IPDT(°C)
G_1	260.0	320.0	310.0	318.8
G_2	210.0	630.4	290.0	435.8

Tab. 6. Decomposition Temperature (DT).

% Weight loss Temp. °C	10%	20%	30%	40%	50%	60%	70%	75%
G_1	262.0	286.0	296.0	300.0	306.0	314.0	348.0	400.0
G_2	150	212.8	221.4	255.6	304.2	461.4	535.7	704.3

Tab. 7. Decomposition Temperature.

Temp. °C (%)Loss Weight	100	200	300	400	500	600	700	800
G_1	3.3	5.0	35.0	75.0	81.0	88.0	92.0	95.0
G_2	3.8	17.7	47.6	49.0	54.1	69.2	75.6	85.6

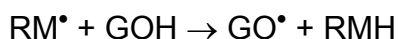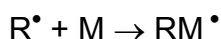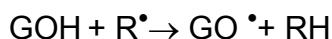Where G_1 = Guar gum, G_2 = Guar gum–g–acrylamide

Mechanism

A mechanism is proposed for the reaction containing guar gum, acrylamide, hydrogen ion, mercaptosuccinic acid and peroxymonosulphate. It was observed that potassium peroxymonosulphate is not capable of producing graft copolymer alone hence R• free radicals are generated by the interaction of peroxymonosulphate and mercaptosuccinic acid. These free radicals abstract hydrogen atom from the guar gum molecule producing guar gum macro radicals (GO˙). The monomer radical which are at the close proximity of the reaction sites become acceptors of the guar gum radicals resulting in chain initiation and thereafter themselves become free radical donor to neighbouring molecules. In this way grafted chain propagates. These grafted chains are terminated by coupling to give graft copolymer.
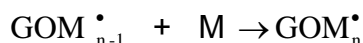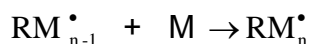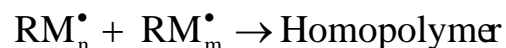
Free radical formation

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Initiation

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

$$R^\bullet + M \rightarrow RM^\bullet$$

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

Propagation

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

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

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

$$RM^\bullet + M \rightarrow RM_1^\bullet$$

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

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

Termination

$$RM_n^\bullet + GOM_n^\bullet \rightarrow \text{Graft copolymer}$$

$$GOM_n^\bullet + GOM_m^\bullet \rightarrow \text{Graft copolymer}$$

$$RM_n^\bullet + RM_m^\bullet \rightarrow \text{Homopolymer}$$
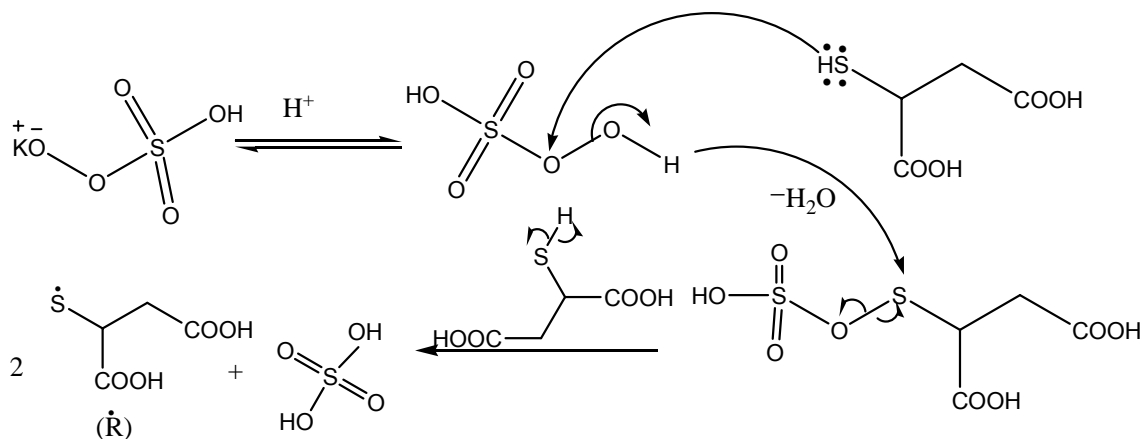
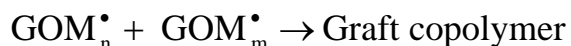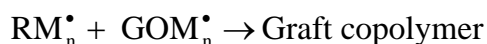## Conclusions

The industrially important graft copolymer guar gum-g-acrylamide was successfully synthesized by using efficient redox initiator i.e. peroxymonosulphate/ mercaptosuccinic acid in inert atmosphere. From all the above study it was concluded that the minimum concentration of redox pair was sufficient for maximum % of grafting which also supports the efficiency of redox pair. It was observed that higher concentration of hydrogen ion retards the grafting onto guar gum. Minimum concentration of guar gum was sufficient for maximum % of grafting while long time and higher temperature favour the grafting on to guar gum. Swelling study provides information that grafted polyacrylamide chain increases the water absorption capacity of polymer backbone. This indicated their applicability as super-absorbent materials. Spectroscopic study proves the grafting of monomer on O–H site of backbone which also supports the proposed mechanism. The higher value of FDT, IPDT and char yield supports the increased thermal stability of graft copolymer and cyclized structure of grafted gum after the removal of NH_3 molecule also supports the high thermal stability. On the basis of previous study it can be concluded that synthesized graft copolymer will behave as good flocculants in comparison to guar gum due to the presence of polyacrylamide chain which is highly stable and show low shear stability.

Experimental part

Materials

Acrylamide (Aldrich, USA) was recrystallized twice from methanol and dried in vacuum. Peroxymonosulphate was received from Aldrich, USA and mercaptosuccinic acid, sulphuric acid, methanol were received from Merck, India and used as such. Guar gum was purchased from Himedia, India.

Synthesis of graft copolymer

Guar gum solution was prepared by adding the desired amount of gum to 100 ml triple distilled water in a three neck reactor and kept in a thermostat at the desired temperature. A definite amount of mercaptosuccinic acid, acrylamide and sulphuric acid solutions were added to the solution. The stream of nitrogen gas was passed into the solution and in peroxymonosulphate solution separately. After the desired time interval, the reaction was initiated by addition of peroxymonosulphate solution of the desired concentration. The reaction has been allowed to continue for the required time after which the reaction mixture was poured into water-methanol mixture. The graft copolymer precipitates out, whereas polyacrylamide remains in the solution. The graft copolymer was separated by filtration and washed with water- methanol mixture (two times) so that any homopolymer stuck to the graft copolymer sample passed into the filtrate. The graft copolymer thus obtained was dried in vacuum oven under vacuum at room temperature and weighed.

Separation of homopolymer

For the separation of homopolymer from the filtrate a pinch of hydroquinone was added to the filtrate and concentrated by distillation under reduced pressure. Thereafter, it is poured into excess of methanol. The polyacrylamide precipitates out which was filtered, dried and weighed and packed into container which was then labelled.

Determination of grafting characteristics

The grafting characteristics was calculated according to Fanta's definition [17] in terms of grafting ratio (%G), Grafting efficiency (%E), Add on (%A), Conversion (%C) and Homopolymer (%H).

$$\%G = \frac{\text{Weight of grafted polymer}}{\text{Weight of substrate}} \times 100$$

$$\%A = \frac{\text{Weight of synthetic polymer}}{\text{Weight of graft copolymer}} \times 100$$

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

$$\%E = \frac{\text{Weight of polymer in graft}}{\text{Weight of polymer formed}} \times 100$$

$$\%H = 100 - \%E$$

Besides the above parameters the rate of grafting (Rg) has was calculated according to following formula [18]

$$Rg = \frac{\text{Weight of grafted polymer(W)}}{\text{Vol.(V)} \times \text{time(T)} \times \text{m. wt. of ACM(M)}} \times 1000 \ (\text{mol l}^{-1}\text{s}^{-1})$$

Where W = Weight of grafted gum - weight of ungrafted gum.

Swelling Study

The swelling behaviour of graft copolymer was carried out in water for an hour and the samples were prepared by varying the concentration of acrylamide. For studying the swelling behaviour the different samples of graft copolymer were taken. These studies were carried out by taking 0.100 gm of graft copolymer in 20 ml of triple distilled water and kept undisturbed for 30 minutes. The surface water on the swollen graft copolymer was removed by safely pressing between the folds of filter paper; an increased in weight has been recorded. Percent swelling (P_S) and swelling ratio (S_R) have been calculated by using following expressions [19] and results are given in Tab. 4.

$$P_S = \frac{\text{Weight of swollen polymer} - \text{weight of dry polymer}}{\text{Weight of dry polymer}} \times 100$$

$$S_R = \frac{\text{Weight of swollen polymer} - \text{weight of dry polymer}}{\text{Weight of dry polymer}}$$

FTIR analysis

For the FTIR spectra 210%G sample was taken and 1mg of sample in 99 mg of KBr was mixed. Pellet was made of the mixture with the thickness of 0.55 mm and radius 6.0 mm and spectra was recorded using a Varian Excaliber series 3000 FTIR model. The IR spectral analysis was utilized to prove grafting.

UV-Visible analysis

The UV–visible spectra of guar gum, acrylamide and guar gum-g-acrylamide (210%G) were recorded in water on PerkinElmer–Lambda 35 UV-VIS Spectrophotometer at room temperature 25 °C. The optical path length of measurement cell was 10 mm and concentration of the solution was 0.1%(w/v).

TGA analysis

The thermal behaviour of guar gum and guar gum-g-acrylamide (210%G) was recorded on NETZSCH –Gerätebäu GmbH thermal analyzer within a temperature range 70 –900 °C in N_2 atmosphere at heating rate of 10 °C/min.

Acknowledgements

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