

Synthesis, Characterization of Modified Guar Gum Copolymers through Graft Copolymerization using Acrylamide and Acrylic Acid and its Effect in Treatment of Crude Oil Emulsified Water

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ABSTRACT

The graft copolymerization of acrylic acid (AA) initiated by potassium persulfate (PPS) progresses through free radical initiation mechanism carried out onto purified guar gum backbone and acrylamide (AM) which has been synthesized by grafting polyacrylamide chains onto carboxymethyl guar gum (CMG) backbone using conventional redox grafting. The graft copolymers were characterized using FT-IR spectroscopy, elemental analysis, thermal analysis, scanning electron microscopy and rheologically. Reverse demulsification performance of the graft copolymers were evaluated using (crude oil-in-water emulsion) sample by a modified jar test method. It showed that graft copolymers based on acrylamide were better reverse demulsifiers than those based on acrylic acid. Among acrylamide synthetic graft copolymers CMG-g-AM (CGA1) diluted to about 1% in a dose of 50ppm performed best when compared with the other synthetic graft copolymers of acrylamide with a reverse demulsification efficiency of 64.7%, while the best reverse demulsification efficiency for graft copolymers of acrylic acid GG-g-AA (GGA2) diluted to about 1% in a dose of 50ppm is 59.2%, both products didn't outperformed the Industrial Reverse Demulsifier (IRD).

KEYWORDS: guar gum, N, N-dimethylacrylamide, acrylic acid, acrylamide, graft copolymerization, oil-in-water emulsion, flocculation

INTRODUCTION

Chemically, guar gum is a polysaccharide composed of the sugars galactose and mannose. The backbone is a linear chain of 1, 4-linked mannose residues to which galactose residues are 1, 6-linked at every second mannose, forming short side-branches. It forms colloidal dispersions with water at room temperature and imparts extraordinary viscosity, because of this property, native guar gum as well as its derivatives are commercially impart and find use in such diverse applications like oil well drilling, paper and textile sizing, as a binding agent for explosives, and is widely used in food industry [1].

Polysaccharides such as starch, chitosan and cellulose have been used for preparing adsorbents [2].

Porous starch-g-poly (acrylic acid) superadsorbent were prepared by free radical graft polymerization

How to cite this paper: Ayman Abu Reid | Yousif. A. Ragab | Salih. MAA | Imad. E. A. Mahajoub "Synthesis, Characterization of Modified Guar Gum Copolymers through Graft Copolymerization using Acrylamide and Acrylic Acid and its Effect in Treatment of Crude Oil Emulsified Water" Published in International Journal of Trend in Scientific Research and Development (ijtsrd), ISSN: 2456-6470, Volume-6 | Issue-5, August 2022, pp.1442-1452, URL: www.ijtsrd.com/papers/ijtsrd50661.pdf



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between AA and potato starch in the aqueous phase by using Triton X-100 as the pore forming agent. The starch-g-poly (acrylic acid) superadsorbent has a porous structure and has the highest adsorption capacity of 1532 mg/g for methylene blue. It is interesting that the adsorption equilibrium can be achieved in 30 min, which is faster than many of the previously reported adsorbents for methylene blue [3].

Grafting reaction of methacrylic acid (MAA) onto guar gum and investigating the effect of reaction temperature, time, initiator concentration, monomer concentration as well as different initiators on grafting parameters. It is the first of its kind of study reported in the literature by using potassium

persulfate (PPS) as an initiator to achieve grafting of MAA onto guar gum [4].

Carboxymethyl guar gum (CMG) is a derivative of guar gum, synthesized by inserting carboxymethyl groups onto the backbone of guar gum [5].

An efficient polymeric flocculent has been crafted by grafting polyacrylamide chains onto carboxymethyl guar gum backbone using redox grafting method. The applicability of these graft copolymers as novel polymeric flocculants for the treatment of simulated wastewater (Kaolin suspension), municipal sewage wastewater and decolourization efficiency of methylene blue dye solution has been reported [6].

Produced water also known as oilfield water can be defined as contaminated water trapped in the reservoir rock and brought up along with oil or gas during production. It is a by-product of the production of hydrocarbons (oil and gas) from underground reservoirs. It consists of formation water which is water naturally present in the reservoir or condensed water in gas production [7]. Besides elevated concentration of heavy metals such as barium, uranium, cadmium, chromium, strontium and lead, produced water contains dispersed oil droplets, dissolved organic compounds and significant amount of anions such as carbonate and bromide sulphate [8].

One of the main requirements in upstream production involves the dehydration of oil to meet pipeline water specifications. Numerous parameters have been cited as playing a role in emulsion stability [9].

In this investigation we examine grafting efficiency of the water-soluble monomers, acrylamide (AM) and acrylic acid (AA) with purified guar gum using potassium persulfate as an initiator. In addition, the resultant copolymers were characterized and its efficiency compared with the industrially used reverse-demulsifier which used in the treatment of oil in water emulsions.

EXPERIMENTAL

A. carboxymethyl guar gum-g-Polyacrylamide (CMG-g-PAM) synthesis.

Solubilization of guar gum in (DMSO/PF)

Materials

dimethyl sulfoxide (DMSO), para formaldehyde (PF) both from SDFCL SD fine-Chem limited, Mumbai-India and purified guar gum.

Method

0.5 gram of purified guar gum and 3 gram of para formaldehyde was dispersed in 50ml DMSO and heated with rapid stirring to 120 C° for 8-15 min. Evolution of formaldehyde occurred and shortly after the onset of vigorous bubbling a clear solution was

obtained, another 3 gram of Para formaldehyde were added to the solution with rapid stirring and heating to 120 C°, after 8-15 minutes evolution of Para formaldehyde occurred and after the onset vigorous bubbling a clear solution was obtained and purified guar gum was dissolved completely [10].

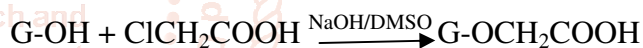
Preparation of carboxymethyl guar gum

Materials

sodium hydroxide, DMSO, mono chloroacetic acid from SDFCL SD fine-Chem limited, Mumbai- India, n-propanol from LOBACHEMIE –Bombay – India, Acetic acid, Ethanol.

Method

Carboxymethylation of purified guar gum followed the same steps which were described by Heinze (2005) for cellulose with some modifications. 4.9 gram of Sodium Hydroxide suspended in 10 ml DMSO was added to the solution of 0.5 gram guar gum in (DMSO/PF) and subsequently 0.88 gram of Mono Chloroacetic acid were added under stirring, the temperature raised to 70 C°, after 4 hours the mixture was cooled to room temperature and put into 150 ml of n-propanol. The solid product was filtered off, dissolved in 40 ml distilled water and neutralized with acetic acid, and precipitated into 70 ml Ethanol, after filtration the product washed with 90% (v/v) Ethanol and dried in oven at 50 C° [11].



Preparation of polyacrylamide grafted carboxymethyl guar gum

Materials

carboxymethyl guar gum was used as synthesized earlier. acrylamide and potassium persulphate was procured from LOBACHEMIE –Bombay – India. Acetone for synthesis (99.0%) from CDH Ltd. New Delhi and hydroquinone were supplied by PIOCHEM for Laboratory Chemicals, Egypt. Acetic acid – extra pure SDFCL SD fine-Chem limited, Mumbai- India. formamide purchased from Fisher Scientific, Bishop Meadow Road, Loughborough, Leicestershire, UK. All the chemicals were used as received, without further purification.

Method

The graft copolymerization of polyacrylamide onto CMG has been carried out in a 100 mL closed system tube. The tube was fitted with an electrically operated magnetic stirrer maintained at temperature 70±1 C°. 0.4 gram (0.0024 mol) of CMG (Calculated on the basis of anhydroglucose unit (AGU). 1 mol of AGU = 162 g.) was dissolved in 80 mL of distilled water with constant stirring and a nitrogen balloon feeding through a needle to deliver nitrogen gas into the reaction system for about 15 min. (5, 7, 9) gram

(0.07, 0.098, 0.13) mol of acrylamide was dissolved in 20 mL of distilled water and mixed with the CMG solution. Afterwards, the solution mixture left for 30 min. At this stage, 0.005 gram of potassium persulphate dissolved in 5 mL distilled water was added under nitrogen gas system the reaction continued for another 1 h, after which it was terminated by adding saturated solution of hydroquinone.

The reaction mixture was stirred at a low constant speed (300 rpm) to avoid the adverse effect of stirring on graft copolymerization. The resultant graft copolymer was precipitated by adding 400 mL of acetone, dried in a hot air oven at 60 °C for 6 h [6].

Purification of the graft copolymer by solvent extraction method

Ungrafting polyacrylamide (PAM) formed by competing homopolymer formation reaction was removed from the graft copolymer by solvent extraction using about 500 ml of a mixture of formamide and acetic acid (1:1 by volume) afterwards the graft copolymer precipitated using 500 ml of acetone, washed and filtered and left to dry on air overnight.

B. Guar gum-g-acrylic acid synthesis.

Materials

purified guar gum, acrylic acid, potassium persulphate all purchased from SDFCL SD fine-Chem limited, Mumbai- India. Acetone for synthesis (99.0%) from CDH Ltd. New Delhi.

Method

The graft copolymer derived from AA and Purified guar gum was prepared by the free radical polymerization. Briefly, 0.5 g of Purified guar gum was dispersed in 30 mL distilled water and dissolved under constant stirring in a closed system tube. Then (0.0582, 0.0655 and 0.0728) mol of AA were mixed with 10 mL of water and added to Purified guar gum solution and stirred for one hour. A quantity of initiator equivalent to (1.14 mmol) dissolved in 10 mL of distilled water and added to the above solution. Polymerization was carried out at 60°C under nitrogen gas atmosphere for 120 min in a thermostatic oil bath under constant stirring. The polymerization product was cooled and poured into excess acetone to induce precipitation. The graft polymer was washed several times with (methanol/water 80: 20 v/v) mixture to remove the homopolymer formed during grafting reaction and the final product dried at 40°C to a constant weight [4].

Measurements

Fourier transform infrared (FT-IR)

FT-IR spectra were acquired on Shimadzu FT-IR 8400 S.CE instrument using potassium bromide

(KBr) discs prepared from a powder samples mixed with dry KBr in the ratio 1: 100. FT-IR spectra were analyzed in the Central Research laboratories, University of Khartoum, all FT-IR spectrums were used as a digital forms except for (PGG) which transformed into a plot form using Microsoft excel 2013.

Elemental analysis (C, H, N)

(C, H, and N) elemental content of purified guar gum were analyzed using Vario EL III instrument, Micro Analytical Center (MAC) Cairo University.

Thermal gravimetric analysis (TGA) and Differential thermal gravimetric analysis (DTG)

Thermo-gravimetric analysis (TGA) was carried out with the help of Thermo Gravimetric and Differential Thermal Analyzer (TGA-50 SHIMADZU/DTG-60H SHIMADZU), Micro Analytical Center (MAC) Cairo University.

Samples were placed in a platinum crucible, weight loss was recorded while the temperature increasing from 0.00 to 600 C° at a rate of 10 C°/min without hold time under a nitrogen flow.

Scanning electron microscopy (SEM)

The microstructure of the sample was characterized by Scanning Electron Microscope at magnification 2000x and 5000x using (SEM, JSM-6610, JEOL, Japan), Micro Analytical Center (MAC) Cairo University.

Rheological behavior

The rheological behavior of diluted aqueous solutions was studied at 25C° using Brookfield DV-III ultra-programmable rheometer, Spindle-21, Density for the same solution was measured using density bottle. National Research Center, Cairo, Egypt.

Reverse demulsification evaluation (Bottle Test)

Samples obtained from (Sudan- Block6 - Bleela oilfield).

Capped glass measuring cylinders 100ml filled with the emulsified water sample to the mark, the made-up solutions of purified guar gum, synthetically modified guar gum, industrial reverse demulsifier and blank (PGG, CGA1, CGA2, CGA3, GGA1, GGA2, GGA3, Industrial reverse demulsifier (IRD), Blank).

The flocculation efficiency of various polymer samples was carried out using modified Jar Test [12]. An emulsified water samples in the prescribed tubes are dosed with (2.5, 5, and 10) µL i.e. (25, 50, and 100) ppm. all tubes were shaken 50 slow rolls and transferred to 60C° water bath and rated immediately after 30min (visually), screening test and its assessment recorded as (Oily, Not oily and Clear) based on best water quality, well-coalesced oil layer

indicating good treatment. After that, using a long needle **10 ml** aliquot taken from the bottom of each tube and tested for oil in water using UV-VIS spectrophotometer.

RESULTS AND DISCUSSION

A. carboxymethyl guar gum-g-polyacrylamide (CMG-g-PAM) synthesis.

% grafting efficiency = (wt. of graft copolymer – wt. of polysaccharide) /wt. of monomer) ×100 (1)

Table 1 carboxymethyl guar gum-g-polyacrylamide (CGA) yields

CM G in g	Acryl amid e in g	K ₂ S ₂ O ₈ in g	Yield	(% G E)	Produ ct code
0.4	5	0.008	5.6	104	CGA1
0.4	7	0.008	2.706 2	32.95	CGA2
0.4	9	0.008	3.41	33.4	CGA3

Evidence of Grafting for the three products

CGA1

On comparing the IR spectra of carboxymethylated guar gum and carboxymethylated guar gum-g-polyacrylamide, there is a peak due to (O-H) stretching vibration and the presence of absorbed moisture at 3429.20 cm⁻¹, its shifting to 3396.41cm⁻¹ in and carboxymethylated guar -g- polyacrylamide might indicate the participation of hydroxyl groups in grafting process. The graft copolymerization is further confirmed by characteristic absorption bands. The (C=O) stretching vibration of primary amide group at 1681.81 cm⁻¹, the peak at 1454.23 cm⁻¹ is the deformation vibrations of aliphatic (C-H) group of monomer molecule, the peak at 1124.42 cm⁻¹ due to (C-N) stretching vibration. The appearance of additional peaks in spectrum of graft copolymer and the great deal of overlapping suggest that grafting might have took place on sites in the carboxymethylated guar gum.

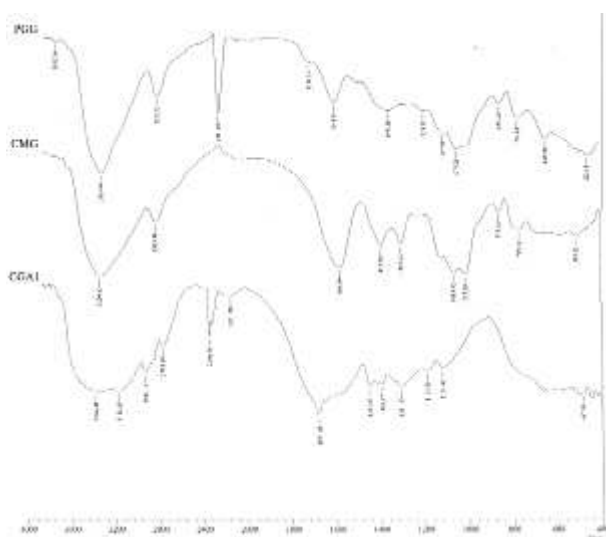


Figure 1 FT- IR spectrum for (CGA1) product

CGA2

On comparing the IR spectra of carboxymethylated guar gum and carboxymethylated guar gum-g-polyacrylamide, there is a peak due to (O-H) stretching vibration and the presence of absorbed moisture at 3400.27 cm⁻¹, its shifting to 3398.34 cm⁻¹ in and carboxymethylated guar -g- polyacrylamide might indicate the participation of hydroxyl groups in grafting process. The graft copolymerization is further confirmed by characteristic absorption bands. The (C=O) stretching vibration of primary amide group at 1681.81 cm⁻¹, the peak at 1452.30 cm⁻¹ is the deformation vibrations of aliphatic (C-H) group of monomer molecule, the peak at 1122.49 cm⁻¹ due to (C-N) stretching vibration. The appearance of additional peaks in spectrum of graft copolymer and the great deal of overlapping suggest that grafting might have took place on sites in the carboxymethylated guar gum.

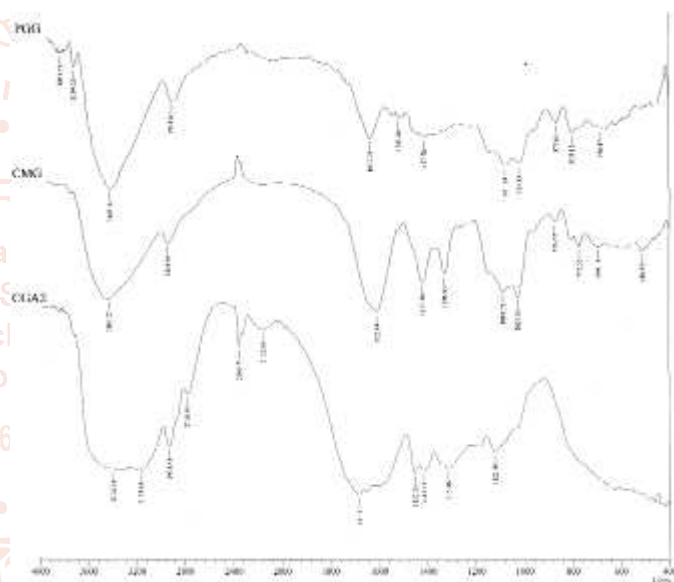


Figure 2 FT- IR spectrum for (CGA2) product

CGA3

On comparing the IR spectra of carboxymethylated guar gum and carboxymethylated guar gum-g-polyacrylamide, there is a peak due to (O-H) stretching vibration and the presence of absorbed moisture at 3411.84 cm⁻¹, its shifting to 3415.70 cm⁻¹ and it's shrinking in and carboxymethylated guar -g- polyacrylamide might indicate the participation of hydroxyl groups in grafting process. The graft copolymerization is further confirmed by characteristic absorption bands. The (C=O) stretching vibration of primary amide group at 1683.74 cm⁻¹, the peak at 1454.23 cm⁻¹ is the deformation vibrations of aliphatic (C-H) group of monomer molecule, the peak at 1120.56 cm⁻¹ due to (C-N) stretching vibration. The appearance of additional peaks in spectrum of graft copolymer and the great deal of overlapping suggest that grafting

might have took place on sites in the carboxymethylated guar gum.

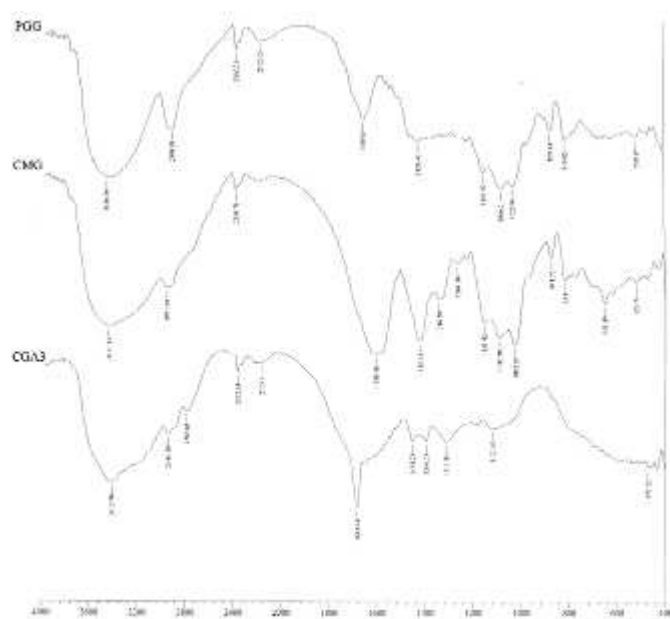


Figure 3 FT- IR spectrum for (CGA3) product

Elemental analysis

The table show the elemental content of Polyacrylamide grafted carboxymethyl guar gum. The contents of (C, H) gradually increased comparing to starting purified guar gum. Meanwhile, the content of (N) was observed to largely increase. These results indicated that the graft copolymerization of polyacrylamide onto carboxymethyl guar gum took place.

Table 2 elemental analysis result for carboxymethyl guar gum-g-polyacrylamide (CGA) products

Sample	C,%	H,%	N,%	O,%
PGG	38.98	7.49	1.14	52.39
CGA1	42.43	8.19	18.59	30.79
CGA2	42.63	8.19	17.54	31.64
CGA3	41.31	8.01	21.17	29.51

Thermal gravimetric analysis (TGA)

Firstly, Thermogram of PGG show three zones of decomposition while CGA thermogram reflects four zones and a slightly lower total weight loss percentage.

Secondly, Comparing of CMG products differential thermal analysis thermogram as a starting material for synthesis of CGA and those of CGA products reveals a beaks at ~380 C° appeared in CGA products, also It has been found that beak degradation of CGA starts at about ~76 C° which is lower than that of CMG products ~100 C° and higher than that of PGG ~90 C° which indicates that graft copolymer is thermally less stable than PGG and its parent CMG.

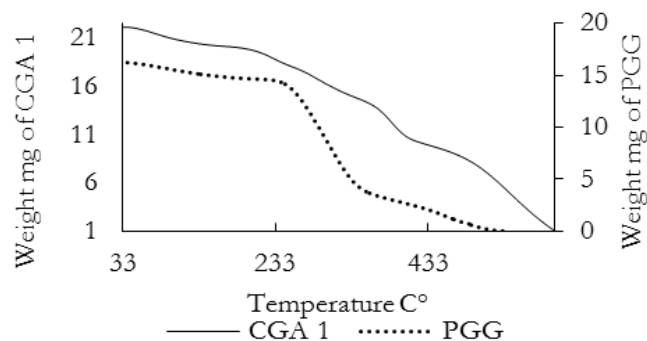


Figure 4 Thermogram of CGA1

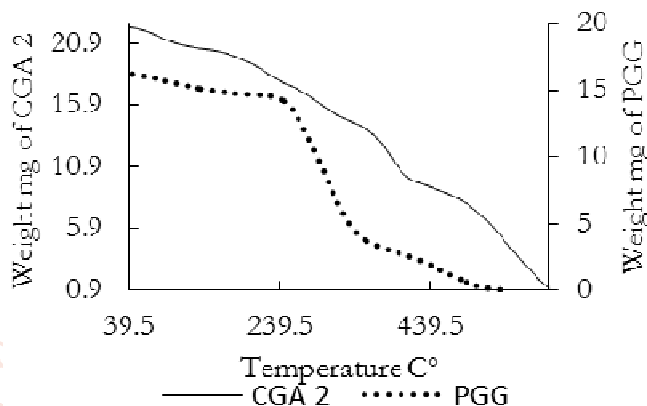


Figure 5 Thermogram of CGA2

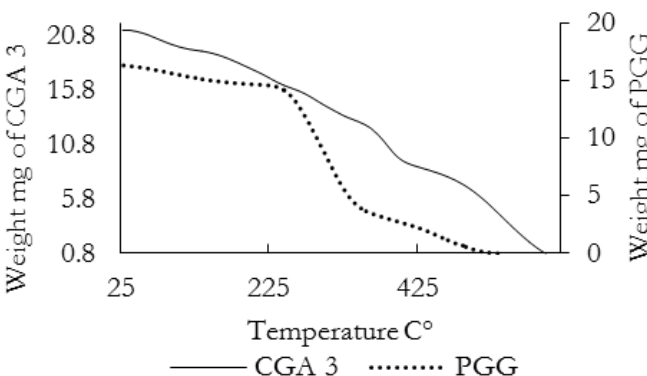


Figure 6 Thermogram of CGA3

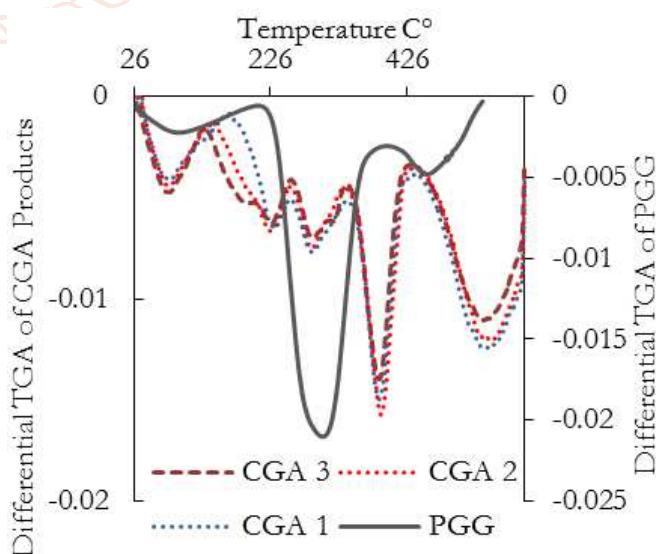


Figure 7 Differential thermogram of (CGA) product

Scanning electron microscopy (SEM)

The morphology of grafted polyacrylamide chains onto carboxymethylated guar gum backbone (CGA)

products is shown in Fig.(b, c and d) at 2000x and investigated for the morphological features against purified guar gum (a). On grafting, the granular smooth appearance of PGG was distorted. This observation suggests that grafting of polyacrylamide affects the structural arrangement of PGG and causes granular disintegration. The micrographs of CGAs showed a unique features where a number of long chain polyacrylamide got agglomerated [6].

It was observed to be as shells, lamellar form structures with cracks, pores and holes developed in accordance with the increase of acrylamide amount.

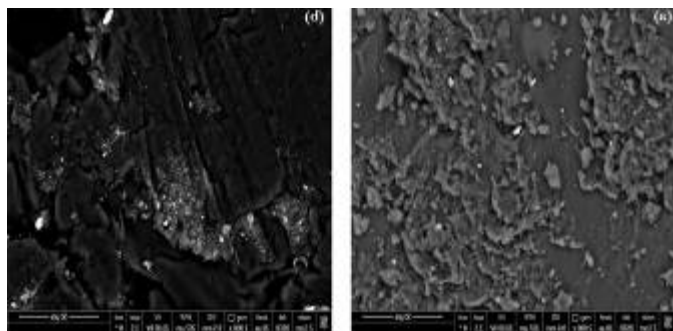


Figure 8 Scanning electron micrographs of purified guar gum (a), CGA1 (b) at (2000x).

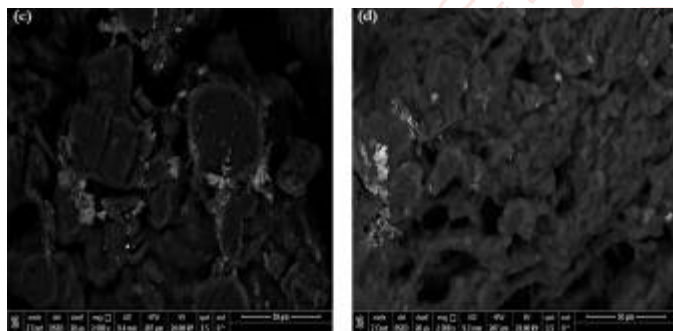


Figure 9 Scanning electron micrographs of CGA2 (c), CGA3 (d) at (2000x).

Rheological behavior

Polyacrylamide grafted carboxymethyl guar gum causes the structure of the long branched chain of purified guar gum to produce a lower viscosity product solutions even at higher concentrations the rheological behavior of (CGA1, CGA2, CGA3) solution diluted to about 1% was studied at 25°C, (%Torque – 2,3,4 respectively,250 rpm). Density for the same solutions was measured using density bottle and gave the values below.

Table 3 Viscosity and density of (GGD4) product and PGG

Sample	Viscosity in centipoise (cP) at 25°C°	Density g/cm ³
PGG	34	0.3757
CGA1	4	0.3602
CGA2	6	0.3779
CGA3	8	0.3722

We noticed an increase in “nitrogen content” from elemental analysis in CGA products on increasing of acrylamide, another result which is related to the appearance of (C=O) stretching vibration of primary amide group around 1650 cm⁻¹ broad band and a clearly increase in viscosity values for CGA products with the same trend, those practical findings support the assumption of grafting taking place and produce a different rheological behavior.

B. Guar gum-g-acrylic acid synthesis.

The grafting efficiency (% GE) calculated by using the following equation:

$$\% \text{ grafting efficiency (\% GE)} = (W1 - W0 / W2) * 100 \dots\dots\dots (2)$$

Where, W0, W1, and W2 denote the weight of PGG, graft copolymer, and monomer, respectively, the table below contain the yields and codes for three products.

Table 4 guar gum-g-acrylic acid (GGA) yields

PGG in grams	Acrylic acid in grams	GGA in grams	% GE	Product code
0.50	4.196	1.805	31.1	GGA1
0.5026	4.7205	1.062	11.8	GGA2
0.5023	5.245	2.8	43.8	GGA3

Grafting percent calculations might be inconvenient because of its weight dependence although it’s high in GGA3, moreover monomer concentration and hence grafting percent might be disturbed by the presence of high homopolymer with the growing grafted chain and it’s expected that swelling of the base polymer at higher monomer concentrations is not favorable for grafting, but we noticed from FT-IR spectrum the presence of carbonyl group although the spectrum is noisy to some extent which supporting the assumption of some disturbance.

Evidence of Grafting for the three products

Grafting of acrylic acid onto purified guar gum was confirmed by studying FT-IR spectrum of GGA products spectrums compared to PGG spectrum.

There is an appearance of a new characteristic absorption band at around (1700 cm⁻¹) in spectrum of GGA products due to carbonyl stretching vibrations of carboxylic acid group. Further, formation of GGA products is supported by the weak intensity of bands at around (3400 cm⁻¹) because of (O-H) stretching vibrations as compared to spectrum of the PGG (3423.41 cm⁻¹), this weakening of the band is due to utilization of some (OH) groups of PGG during the formation of the graft copolymer, similar findings were observed by Kang et. al [13].

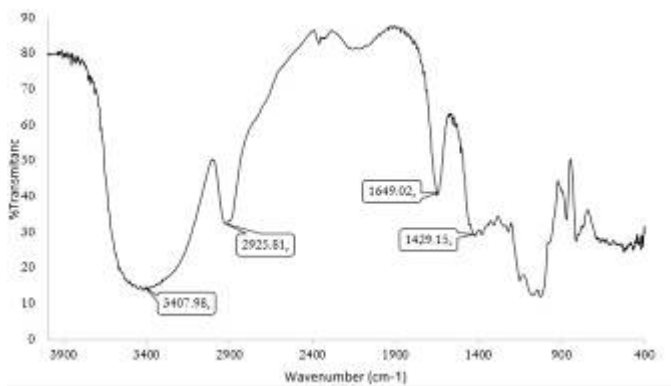


Figure 10 FT-IR spectrum of purified guar gum (PGG)

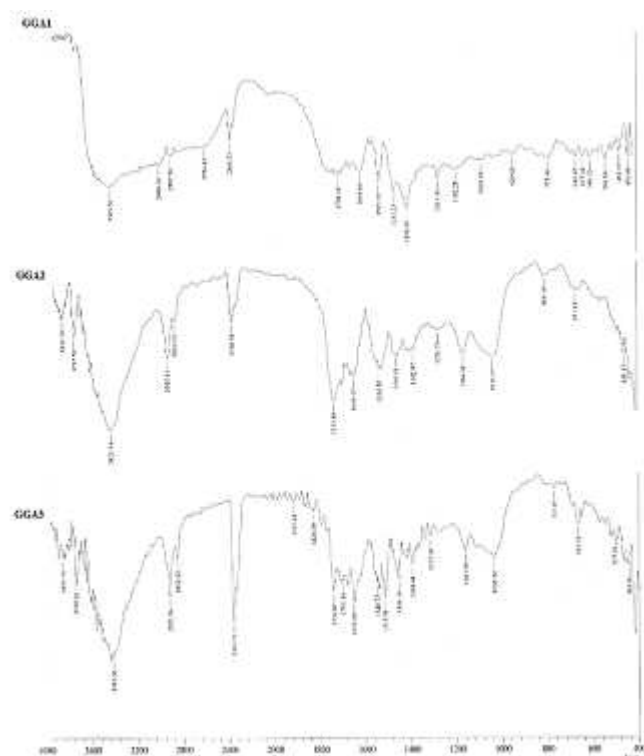


Figure 11 FT- IR spectrum for (GGA) products

Elemental analysis

The table show the elemental contents of grafting product of acrylic acid onto guar gum. It can be seen in the table that the contents of (C) increased compared to starting purified guar gum. Meanwhile, the content of (H, O) was observed to decrease which suggest some degradation.

Table 5 elemental analysis result for guar gum-acrylic acid (GGA) products

Sample	C, %	H, %	N, %	O, %
PGG	38.98	7.49	1.14	52.39
GGA1	45.18	6.50	2.09	46.23
GGA 2	44.74	6.46	1.7	47.1
GGA 3	45.49	7.07	1.648	45.792

Thermal gravimetric analysis (TGA)

Generally, GGA products experienced a massive weight loss (73.169, 72.968 and 81.039 %) at ~240 C°, it's the polymer decomposition temperature (PDT), degradation of GGA products started at slightly higher temperature than PGG and shows three degradation steps. On comparing the thermo gram of parent backbone and graft copolymer GGA products, it has been observed that total weight loss percent for PGG and GGA products lays in the same range which indicates that graft copolymer is thermally stable like its parent backbone.

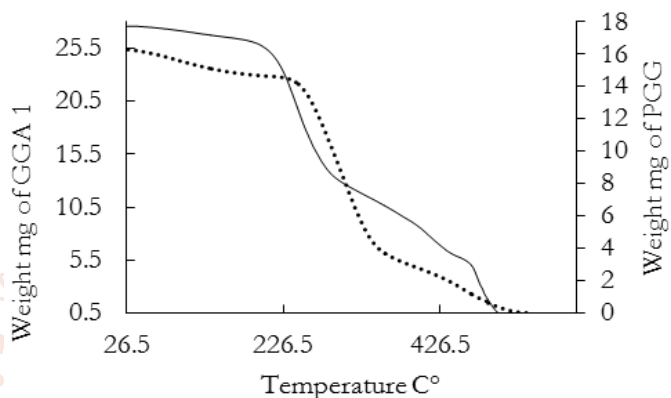


Figure 12 Thermogram of GGA1

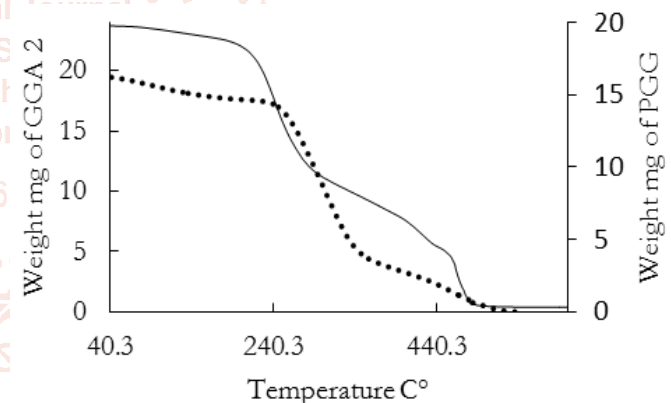


Figure 13 Thermogram of GGA2

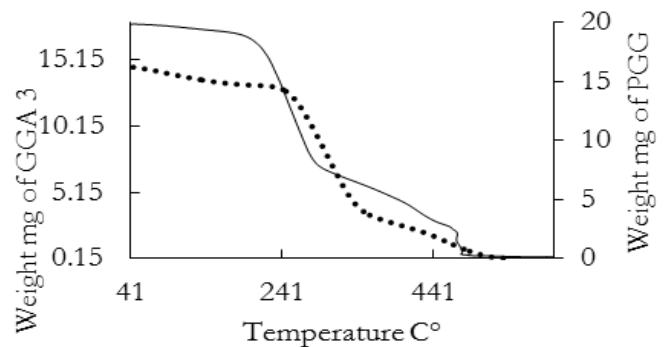


Figure 14 Thermogram of GGA3

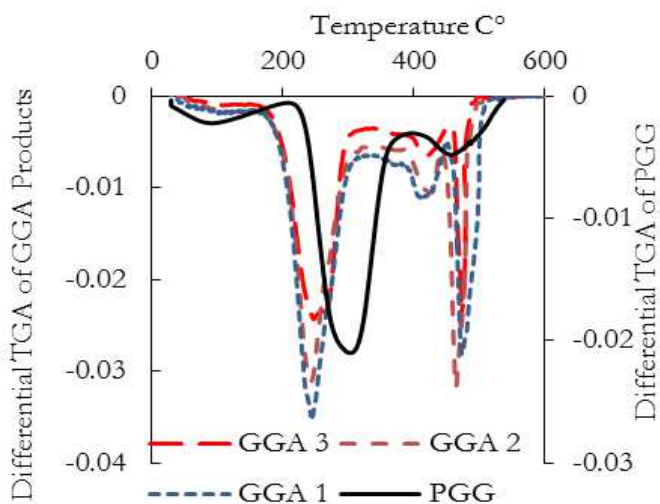


Figure 15 Differential thermogram of (GGA) product

Scanning electron microscopy (SEM)

The morphology of (GGA) products is shown in Fig.(b, c and d) at 5000x and investigated against purified guar gum (a). Purified guar gum of this magnification show a compacted but scaly, rough, porous and cracked surface. Grafted products show a slightly smooth surface and particles on top, which get fibrous and irregular with the change in oxygen content and hence the acrylic acid amount. Graft copolymerization between purified guar gum and acrylic acid formed throw a crosslinked network [3].

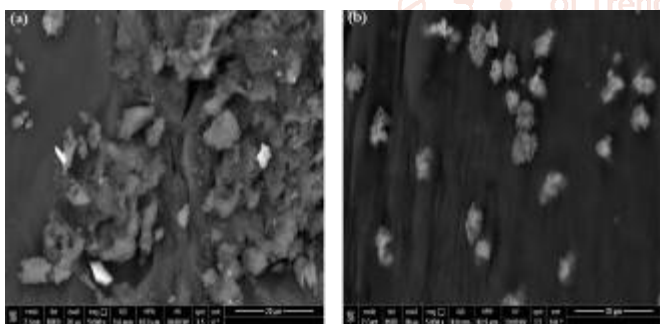


Figure 16 Scanning electron micrographs of purified guar gum (a), GGA1 (b) at (5000x).

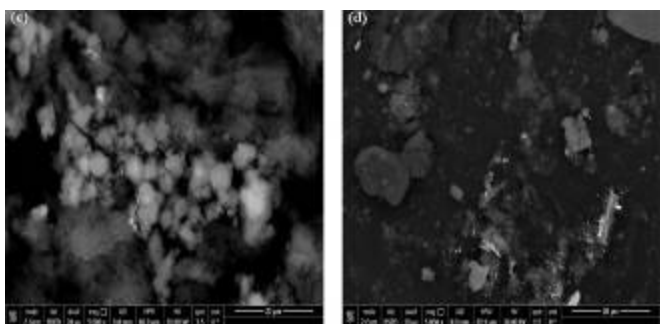


Figure 17 Scanning electron micrographs of GGA2 (c), GGA3 (d) at (5000x).

Rheological behavior

Grafting of acrylic acid onto guar gum causes the structure of the long branched chain of purified guar gum to produce a lower viscosity product solutions even at higher concentrations the rheological behavior of (GGA1, GGA2, GGA3) solution diluted to about

1% was studied at 25C°, Spindle-21, (%Torque – 23.6, 24.6, 25.6 respectively, 250 rpm). Density for the same solutions was measured using density bottle and gave the values below.

Table 6 Viscosity and density of (GGA) product and PGG

Sample	Viscosity in centipoise (cP) at 25C°	Density g\cm3
PGG	34	0.3757
GGA1	4.3	1.04
GGA2	4.6	1.04
GGA3	4.8	1.04

Visual and spectrophotometric evaluation

With a dose of 2.5µL or 25ppm, visual evaluation reveled a slight difference could be seen across samples except for the sample (IRD) Industrial reverse demulsifier which show no oil droplets on the glass sides and looked clear, samples show some oil droplets on the glass sides are described as not-oily like (CGA1), on the other hand, very high oil-in-water concentrations appeared in UV-VIS spectrophotometer readings for samples (GGA1, GGA2 and GGA3) even higher than the blank sample which might give a sing for emulsion formation.

With a dose of 5µL or 50ppm, visual evaluation reveled there is a slight difference could be seen across samples except for sample (IRD) industrial reverse demulsifier which show no oil droplets on the glass sides and looked clear, samples show some oil droplets on the glass sides are described as not-oily like (CGA1, CGA3) but high oil-in-water concentrations appeared in UV-VIS spectrophotometer readings for samples (PGG) but not higher than blank which might give a sing for no emulsion formation but in contrast almost all products developed some emulsion breaking characteristics.

With a dose of 10µL or 100ppm, visual evaluation reveled there is a slight difference could be seen across samples except for sample except for sample (IRD) industrial reverse demulsifier which show no oil droplets on the glass sides and looked clear, samples show some oil droplets on the glass sides are described as not-oily, but a high oil-in-water concentrations appeared in UV-VIS spectrophotometer readings of samples (GGA1, GGA2 and GGA3) and even higher than the blank sample which might give a sing for emulsion formation.

Generally, its worthy to say that best results of oil in water concentration and hence highest deoiling efficiency was accomplished with the Industrial reverse demulsifier, but for guar gum products the efficiency have been noticed with a dose of 2.5µL or

25ppm of (CGA2) product which gives a deoiling efficiency of (32.5) respectively and with a dose of 5µL or 50ppm of (CGA1, GGA2 and CGA3) products, the deoiling efficiency increased to reach (64.7, 59.2, 54) respectively and finally with a dose of 10µL or 100ppm of (GGA3) which gave an efficiency of (23.3). Hence we can conclude that (CGA1, CGA2 and GGA2) are the synthetically modified guar gum products with the best reverse demulsification (deoiling) properties using a dose of 2.5µL or 25ppm.



Figure 19 visual evaluation of 50 ppm dose deoiling efficiency



Figure 20 visual evaluation of 100 ppm dose deoiling efficiency



Figure 18 visual evaluation of 25 ppm dose deoiling efficiency

Table 7 Spectrophotometric evaluation of purified guar gum and its derivatives deoiling efficiency

Sample code - Dilution %	Doses in µL	O/W in PPM	De-oiling Efficiency
PGG - 0.04%	2.5	320	13.3
	5	277.5	18.4
	10	244.8	0
CGA1 - 1%	2.5	298	19.2
	5	120	64.7
	10	306	1.3
CGA2 - 1%	2.5	249	32.5
	5	187.5	44.9
	10	293	5.5
CGA3 - 1%	2.5	304	17.6
	5	155.3	54
	10	281	9.3
GGA1- 1%	2.5	416	0
	5	157.6	53.6
	10	328	0
GGA2- 1%	2.5	532	0
	5	138.8	59.2
	10	326	0
GGA3- 1%	2.5	432	0
	5	185	45.6
	10	238	23.3
IRD	2.5	40	89.1
	5	58.8	82.8
	10	44	85.5
Blank	2.5	369	0
	5	340	0
	10	310	0

DE-OILING EFFICIENCY

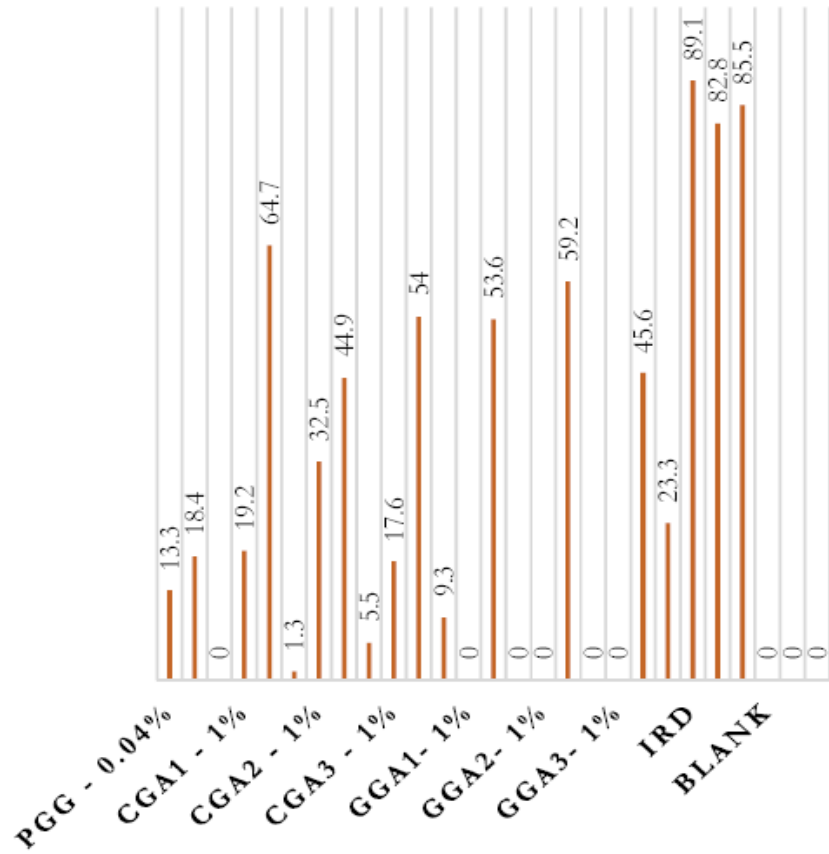


Figure 21 de-oiling efficiency of all samples

OIL IN WATER IN PPM

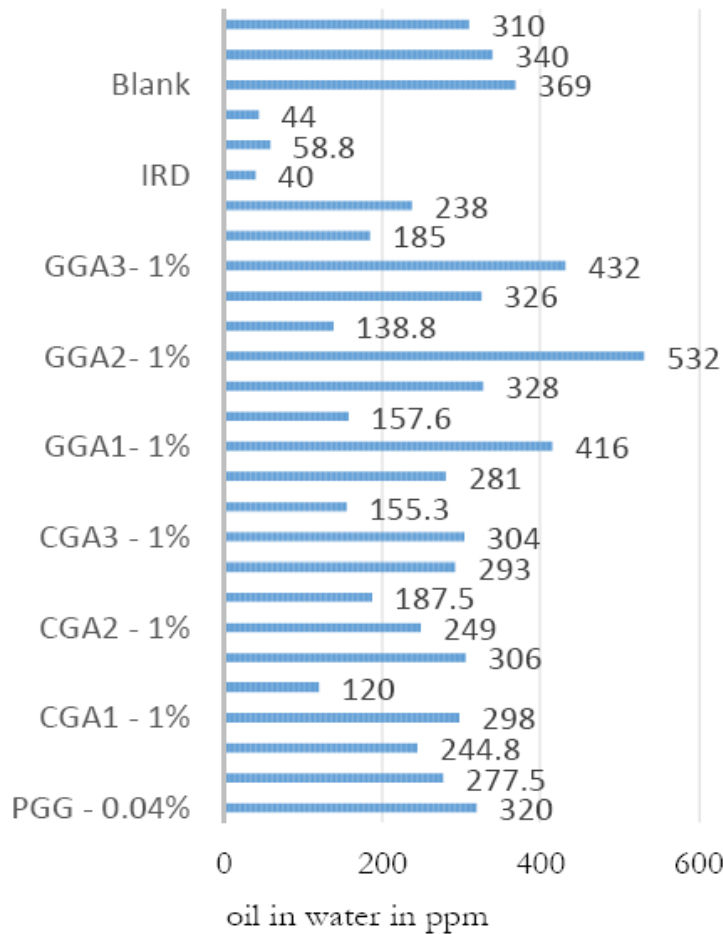


Figure 22 oil-in-water in ppm

CONCLUSION

Reverse demulsification efficiency of carboxymethylated guar gum, carboxymethyl guar gum-g-acrylamid have been investigated earlier on kaolin suspension and municipal sewage wastewater and gave an efficiency, our targeted wastewater (emulsified water) produced from oil field demulsified the same way which is a confirmation of the ability of these products.

We can conclude that application of low concentrations of the above mentioned products with a low dose (5 μ L or 50 ppm) exhibit a deoiling efficiency of (64) percent for CGA1 and on increasing the dose volume we experienced some emulsification which expected from the parent backbone (guar gum) characteristics.

As indicated from this work results, fine grades of guar gum or preferentially purified guar gum can be more developed and utilized in reverse-demulsification (deoiling) processes throw grafting and benefited from some of its preserved biodegradability as it gives a chance to the bacterial growth to take over the rest.

Easy to form products and much diluted solutions for reverse-demulsification is favored, so it is valuable environmentally and economically.

Pilot plants could be constructed in the oilfields to produce such products and assure its freshness and improve its efficiency according to crude oil type.

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