

Ceric Ammonium Nitrate Induced Grafting of 3,3-Dimethyl Acrylic Acid onto Gum Arabic

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ABSTRACT

This experiment is a continuation of our effort to develop drug delivery carrier of Gum Arabic GA (Acacia Senegal) Gum Arabic-g-3,3-dimethyl acrylic acid for a cancer. The effect of graft reaction conditions on the percentage of graft efficiency and percentage of graft yield in the graft copolymerization were investigated. It was observed that grafting parameters such as 3,3-dimethyl acrylic acid, ceric ammonium nitrate (CAN), Gum Arabic (GA), temperature and reaction time have remarkable influence on the percentage of graft efficiency and percentage of graft yield of the graft copolymer. The optimum percentage of graft efficiency and percentage of graft yield were (26%) and (75.5%). Evidence of grafting was confirmed by comparison of FTIR spectra of GA, 3,3-dimethyl acrylic acid and the grafted copolymer as well as scanning electron micrography (SEM), Thermogravimetric analysis (TGA) and X-ray diffraction of the product.

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Introduction

Gum Arabic or gum acacia, locally known as gum 'Hashab', is the most widely used and traded of the true water soluble gums. True Gum Arabic is produced by Acacia Senegal only, but gums obtained from other Acacias are also sometimes, though erroneously, referred to by the same name. Gum Arabic came to medieval Europe through Arabs, hence the name, gum arable.

Gum Arabic (GA) is a natural composite polysaccharide rich in non viscous soluble fiber and derived from exudates of Acacia Senegal and Acacia Seyal trees. GA from Acacia Senegal is a complex branched heteropolyelectrolyte with a backbone of 1,3-linked β -galactopyranose units and side-chains of 1,6-linked galactopyranose units terminating in glucuronic acid or 4-O-methylglucuronic acid residues [1,2]. GA consists of three fractions with distinct chemical structures, where the major one is a highly branched polysaccharide with a molecular weight of 3×10^5 g/mol; about 10% (wt) of the total is a high molecular weight arabinogalactan protein complex (1×10^6 g/ml) and around 1% (wt) of the total contains the highest protein content (.50 wt %). The protein in GA is rich in hydroxypropyl, prolyl and seryl residues covalently linked to carbohydrate moieties [3]. The arabinogalactan-protein complexes contain several polysaccharide units linked to a common protein core forming a compact spheroid structure according to the "wattle-blossom" model [2]. Another model for the structure of GA indicates the polysaccharide-protein complex as a twisted hairy rope of 150 nm length and 5 nm diameter [5]. Although the structure of the complex has not been fully resolved, it is possible to reconcile the two models [6] GA possesses remarkable surface active and rheological properties, being suggested that the emulsifying activity of GA is mostly due to its protein content and to trace levels of lipids [4,6,7]. At present, GA is generally recognized as safe [8], and has wide

applications as a stabilizer, thickening agent and hydrocolloid emulsifier, mostly used in food industry, but also in the textile, pottery, lithography, cosmetics and pharmaceutical industries [9]. Several researchers are also studying the application of GA in the development of controlled drug delivery systems [10, 11, 12], and carriers for the microencapsulation of oils and other bioactive molecules [13, 14, 15]. Recently, the use of GA has been extended to the nanotechnology and nanomedicine fields, due to its biocompatibility for in vivo applications, as well as its stabilization of nanostructures. As it is a highly branched polysaccharide with high contents of galactose, it has been proved to interact with asialoglycoprotein receptors of hepatocytes. GA has been probed for the coating and increase biocompatibility (in vitro and in vivo studies) of iron oxide magnetic nanoparticles [16, 20], gold nanoparticles [21, 22], carbon nanotubes [23,24] and quantum dot nanocolloids [25].

For the last few decades, chemical modification of Gum Arabic by graft copolymerization of vinyl monomers onto it has been a subject of academic as well as industrial interest [26].

Materials and Methods

Materials

Gum Arabic (Acacia Senegal) was used in this study. It was obtained from Arabic Gum Company Ltd, Sudan, in spray-dried. Also other materials were used such as: 3,3-dimethyl acrylic acid, puriss, Ceric Ammonium Nitrate (CAN), Nitric Acid (Molar Solution) and Ethanol, all were supplied from purum (Fluka Co.).

Equipments

The equipments used in this study were

(1) - Fourier transform infrared spectrometer (FT-IR), model Perkin Elmer 2000 FT-IR system supplied from (Perkin Elmer, Norwalk, CT), using the KBr disk method (2 mg

sample in 200 mg KBr). The scanning range was 500 to 4000 cm^{-1} and the resolution was 1 cm^{-1} .

(2) - X-ray Diffraction system attached with liquid nitrogen cooled detector, model Bruker D 8 Advance (Germany), equipped with a θ - θ goniometer under the following operation conditions: 40 KV and 40 mA with $\text{CuK } \alpha$ -radiation at $\lambda 1.54056 \text{ \AA}$. The relative intensity was recorded in the scattering range (2θ) of 4 – 60° ,

(3) - Scanning Electron Microscope (SEM), supplied from JEOL (Japan) model 840 A°

(4) - Thermogravimetric analysis system (TGA) supplied from Shimadzu (Japan) at a heating rate of $10^\circ\text{C}/\text{min}$.

Methods

Synthesis of Graft Copolymer

The graft copolymerization of 3,3-dimethyl acrylic acid onto Gum Arabic was carried out under different reaction conditions and different concentrations of the monomer to obtain the optimum condition of graft copolymerization. In this study the graft copolymerization method was done as follows:

0.5 gram of gum Arabic was dissolved in 75 mL of double distilled water, then it was magnetically stirred under nitrogen for 5 minutes, followed by the addition of required amount of Cerium IV ammonium nitrate (CAN) in molar nitric acid with continuous stirring for 15 minutes to facilitate the formation of free radical sites on the Gum Arabic chain followed by drop wise addition of 3,3-dimethyl acrylic acid. The total volume was completed to 100 mL by distilled water. Then the polymerization process was preceded at 30°C for 3 hours. After that solution was allowed to cool, the mixture was washed with water and ethanol repeatedly to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The grafted copolymer was dried under vacuum oven at 40°C to a constant weight and its percentage of grafting efficiency (%GE) and percentage of grafting yield (%GY) were deduced according to the following equations [27]:

$$\% \text{Graft Efficiency} (\% \text{GE}) = 100(W_2 - W_1) / W_1 \quad (1)$$

$$\% \text{Graft yield} (\% \text{GY}) = 100(W_2 - W_1) / W_3 \quad (2)$$

Where W_1 , W_2 and W_3 denote, the weights of the natural polymer, graft copolymer and monomer, respectively.

Results and Discussion

Effect of Monomer Concentration

The effect of monomer (3,3-dimethyl acrylic acid) on the percentage of graft efficiency and percentage of graft yield of GA-g-3,3-dimethyl acrylic acid is shown in figure (1) the percentage of graft yield increases initially over the monomer range of 0.01 to 0.02 mol dm^{-3} and then decreases. The percentage of graft yield at the optimum monomer concentration of 0.02 mol dm^{-3} was 75.5%, while the percentage of graft efficiency at the same concentration was 26%. The apparent acceleration in the percentage of graft yield and percentage of graft efficiency may be attributed to the gel effect, resulting from an enhanced solubility of poly3,3-dimethyl acrylic acid in the monomer [28]. This would consequently increase the viscosity of the reaction medium and reduce rate of termination by coupling the growing polymer chains. The decrease in the percentage of graft yield and percentage of graft efficiency at a monomer concentration higher than 0.02 mol dm^{-3} may be due to an enhanced homopolymer formation by chain transfer to monomer [29].

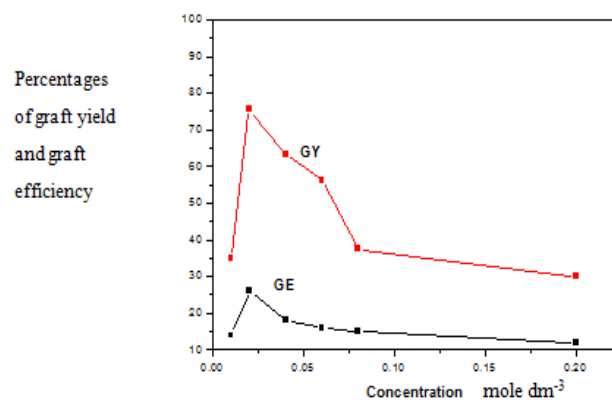


Fig 1. Effect of monomer concentration on %GE and %GY of GA-g-3,3-dimethyl acrylic acid ($\text{CAN} = 0.91 \times 10^{-3} \text{ mol dm}^{-3}$ in 100 ml solution, at 30°C).

Effect of Initiator Concentration

Figure (2) shows the effect of initiator (CAN) concentration on graft efficiency and graft yield of GA-g-3,3-dimethyl acrylic acid. At very low concentration, $0.85 \times 10^{-3} \text{ mol dm}^{-3}$, percentage graft yield and percentage graft efficiency was found to be 66.4%, 22.9% respectively. With increasing concentration of the initiator to $0.91 \times 10^{-3} \text{ mol dm}^{-3}$ percentage graft yield and percentage graft efficiency increase to 75.5%, 26.0%, respectively. Further increases in concentration of (CAN) leads to a reduction in percentage graft yield and accordingly the percentage graft efficiency. The initial increase may be due to an increase in the concentration of free radicals in the system. At a critical initiator concentration of $0.91 \times 10^{-3} \text{ mol dm}^{-3}$, there is a possibility of reversal reaction of grafted polymeric radicals [27,30].

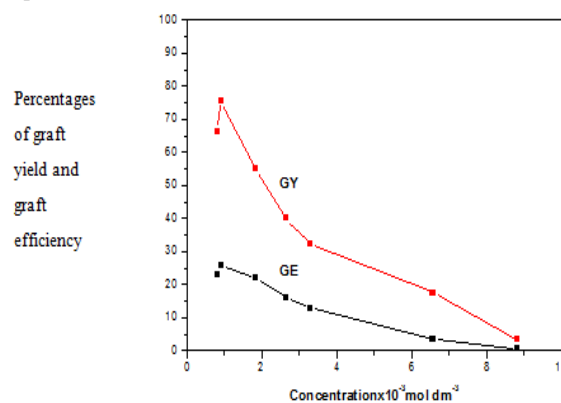


Fig 2. Effect of Initiator concentration on %GE and %GY of GA-g-3,3-dimethyl acrylic acid ($3,3$ -dimethyl acrylic acid $= 0.020 \text{ mol dm}^{-3}$ in 100 ml solution, at 30°C).

Effect of Temperature

The effect of temperature on graft copolymerization was investigated in temperature range between 20 – 50°C . Figure (3) indicates initial increases in percentage graft yield and percentage graft efficiency up to 30°C followed by a gradual decrease above 30°C . The percentage graft yield and percentage graft efficiency increase, with temperature in the range of 20 - 30°C and decreases with increasing of temperature. This may be due to an increase in swellability of the polysaccharide (GA) and enhanced rate of diffusion of the monomer to the radical sites on the GA and on the graft polymer [27,30,31].

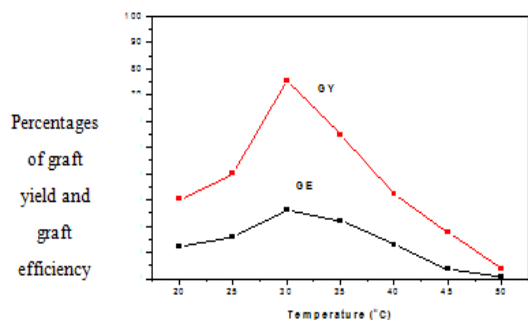


Fig 3. Effect of temperature on %GE and %GY of GA-g-3,3-dimethyl acrylic acid (3,3-dimethyl acrylic acid =0.020 mole dm^{-3} , CAN=0.91 $\times 10^{-3}$ in 100 ml solution.

Effect of Time

The time conversion curve of graft copolymerization is represented in figure (4) the graph is characterized by initial increases in percentage graft yield and percentage graft efficiency with time up to 3 hours after which the yield decreases with time. This result agrees with earlier report by Eromosele and Hamagadu [28]. The decrease in percentages graft yield and percentage graft efficiency after 3 hours may be rationalized by partial hydrolysis and dissolution of the grafted polymer chains [32].

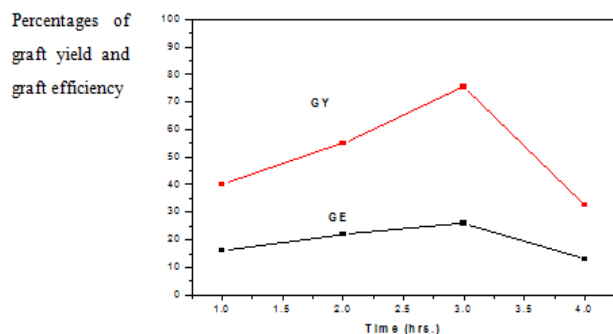


Fig 4. Effect of time on %GE and %GY of GA-g-3,3-dimethyl acrylic acid

Effect of GA Concentration

The effect of GA concentration on percentage graft yield and percentage graft efficiency of GA-g-3,3-dimethyl acrylic acid is presented in figure (5). It is revealed that percentages graft yield and percentage graft efficiency initially increased and then decreased. The initial, increases can be rationalized by the increases in GA concentration. The observed trend at higher concentration may be due to increase in homopolymerization. It may also be as a result of caging effect [32].

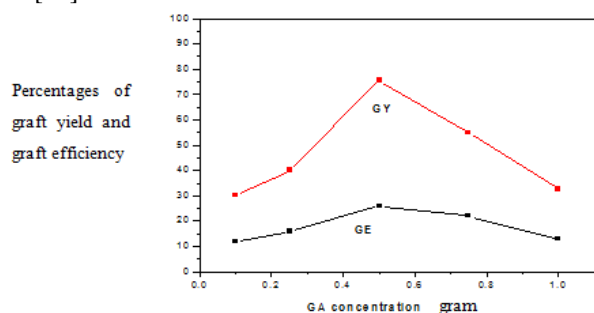


Fig 5. Effect of concentration of GA on %GE and %GY of GA-g-3,3-dimethyl acrylic acid (3,3-dimethyl acrylic acid =0.020 mole dm^{-3} , CAN=0.91 $\times 10^{-3}$ in 100 ml solution, Time 3 hrs. and at 30°C)

FTIR of GA-g-3,3-Dimethyle Acrylic Acid

As maintained above the evidence of grafting has been obtained during the graft copolymerization of different ratios

of 3,3-dimethyle acrylic acid onto GA, from the increases in weight of the product of the graft copolymer compared with the original substrate. Also the evidence of grafting was observed among the infrared spectra comparison between the substrate and graft copolymer. Figure (6) presents the FTIR of Gum Arabic, 3,3-dimethyle acrylic acid and Gum Arabic grafted 3,3-dimethyle acrylic acid. The figure shows the main vibration bands of unmodified Gum Arabic, 3,3-dimethyle acrylic acid and GA-g-3,3-dimethyle acrylic acid, respectively.

The Gum Arabic showed a broad absorption band at 3420 cm^{-1} . This band is characteristic of the glucosidic ring and might due to the stretching vibration of O-H. Also there is a peak at 2933 cm^{-1} , attributed to the C-H stretching vibration.

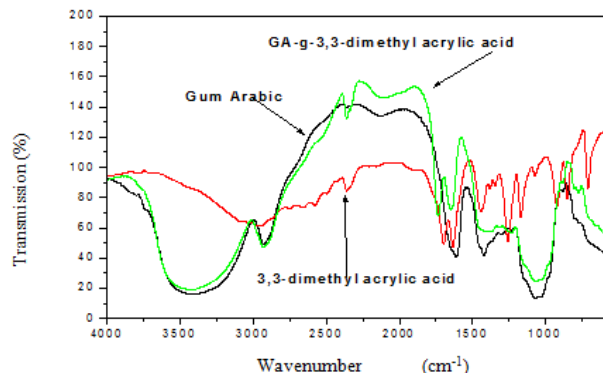


Fig 6. FTIR spectra of GA, 3,3-dimethyle acrylic acid, and GA-g-3,3-dimethyle acrylic acid in the range from 4000 to 500 cm^{-1}

In addition, the bands at 3035 and 2812 cm^{-1} are attributed to the symmetric stretching of C-H₂ and vibration of stretching $\nu\text{C-H}$. When the Gum Arabic was grafted by 3,3-dimethyl acrylic acid the FTIR spectrum of the grafted copolymerized product showed the same absorption bands as in case of Gum Arabic within the region 4000-2750 cm^{-1} . In case of 3,3-dimethyl acrylic acid, the recorded infrared spectra were carried out between 4000-500 cm^{-1} . The broad absorption band of 3,3-dimethyl acrylic acid has maximum absorption characteristic located at 2949 cm^{-1} for O-H stretching band. The weak peak observed at 2350 cm^{-1} is considered to the CO₂ vibration. The peaks between 1698 cm^{-1} and 1629 cm^{-1} are due to the $\nu\text{C=O}$, the C=C stretching and in plan bending of C-H₂, while the band at 1428 cm^{-1} is due to the in plan bending of C-H₂. Analysis spectra shows that the bands between 1257-1064 cm^{-1} assigned to C-O stretching vibrations, while the bands at 988 and 961 cm^{-1} are assigned to plan bending CH₂. When Gum Arabic grafted with 3,3-dimethyl acrylic acid we observed presence of an additional sharp peak at 2350 cm^{-1} , indicated that the grafting had taken place. This peak might be assigned to the CO₂ vibration. The study of the spectrum in the region between 2000-1250 cm^{-1} illustrated that the FTIR of Gum Arabic and showed a strong peak at 1610 cm^{-1} which attributed to the COO asymmetric stretching. When Gum Arabic was grafted with 3,3-dimethyl acrylic acid, another additional peak is appeared at 1737 cm^{-1} and the strong peak of Gum Arabic at 1610 cm^{-1} was shifted to 1645 cm^{-1} . The shift of this band and the appearance of another extra new band at 1737 cm^{-1} suggest the existence of grafting. The 3,3-dimethyl acrylic acid has two peaks in the same region at 1698 cm^{-1} , 1629 cm^{-1} , these two peaks are due to the $\nu\text{C=O}$, C=C stretching and in plan bending of C-H₂. The shift of these two peaks to 1737 cm^{-1} and 1645 cm^{-1} are elucidated to the grafting. In the range of 1250-500 cm^{-1} the FTIR spectrum shows that the vibrational bands of 3,3-

dimethyl acrylic acid are disappeared. It can be observed that the variations between untreated Gum Arabic and grafted Gum Arabic are similar with a decreasing in the optical density of the bands of grafted Gum Arabic. It is also observed that there is an increasing in the optical density of all other shoulders at 880, 802 and 774 cm^{-1} , was for grafted Gum Arabic. This indicated that the Gum Arabic was grafted by 3,3-dimethyl acrylic acid.

X-ray Diffraction (XRD) of GA and Gum Arabic-g-3,3-Dimethyl Acrylic Acid

Fig. (7-a,b) illustrated the powder X-ray diffractograms obtained for natural GA, before and after grafting, respectively. The XRD pattern shows the amorphous nature of GA. From figure (7a), the maximum intensity was obtained at $2\theta = 19.895^\circ$ (θ is the angle of incidence). The observed peak corresponds to $2\theta = 19.895^\circ$, has the average grain length estimated to $d\text{-space} = 4.4375\text{\AA}$. The XRD pattern provides an interesting feature of intensity distribution. After carrying out the graft copolymerization of GA with 3,3-dimethyl acrylic acid, the peak was shifted considerably to $2\theta = 20.32^\circ$ which has the average grain length estimated to $d\text{-space} = 4.279\text{\AA}$. On the other side, fig.(7b) shows that the was grafting decreases the intensity of the corresponding peak. The graft copolymerized sample become almost amorphous. The grafting of 3,3-dimethyl acrylic acid taken place randomly along the GA chain, giving rise to a random copolymer. This destroyed the regularity of the packing of the original GA chains, which result the formation of amorphous copolymer.

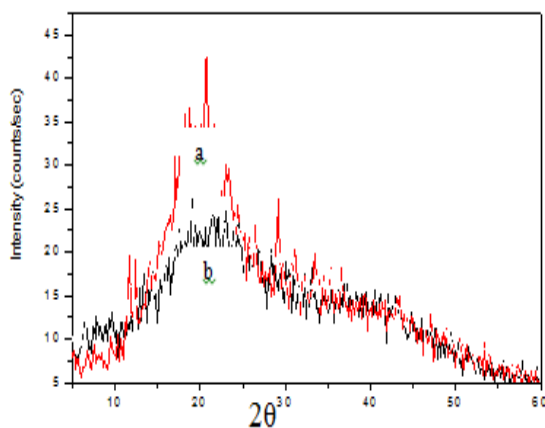


Fig 7-a,b. XRD of (a) Gum Arabic and (b) Gum Arabic-g-3,3-dimethyl acrylic.

Scanning Electron Microscope (SEM) of GA and GA-g-3,3-dimethyl acrylic acid

Morphological examination of the fine powder of Gum Arabic and grafted copolymerized was carried out using SEM type (JEOL-840) by making a thin film of desirable size on copper grids and coated with gold. The surface topography of the GA-g-3,3-dimethyl acrylic acid was studied by SEM and compared with the GA. The exterior surface of the GA-g-3,3-dimethyl acrylic acid appears as irregular rocky surface and clearly different from that of the parent GA, which has spherical shape with many dents on the surface. Hence, the surface evidence supports the grafting of 3,3-dimethyl acrylic acid onto the GA as shown in Fig.(8-a,b).

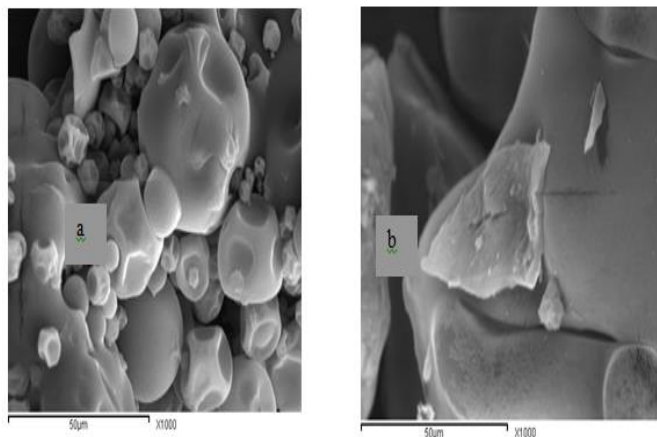


Figure 8-a,b. Typical SEM images of (a) Gum Arabic before grafting and (b) GA-g- 3,3-dimethyl acrylic acid.

Thermogravimetric Analysis (TGA)

Gum Arabic-g-3,3-dimethyl acrylic acid

In this study TGA was done on the dried samples in air with a heating rate of $10^\circ\text{C}/\text{min}$. Figure (9-a,b) and table (1) illustrate the details of thermal behavior according to the primary thermograms and derivative thermograms for Gum Arabic and Gum Arabic-g-3,3-dimethyl acrylic acid. The samples showed first a small weight loss (9%) up to 215°C and (8%) up to 180°C for GA and GA-g-3,3-dimethyl acrylic acid, respectively. The early minor weight loss in samples is attributed to desorption of moisture as hydrogen bound water to the saccharide structure. This is not unexpected taking into account the hydrophilic nature of the composite constituents. It should be noted that the thermogram of the Gum Arabic exhibited four stages of decomposition patterns. On the other hand, GA-g-3,3-dimethyl acrylic acid composite is very similar to that of pure Gum Arabic. This means that the thermal stability of the composite is determined by the degradation of the stabilizer. The thermal resistance of GA-g-3,3-dimethyl acrylic acid was determined by TGA taking GA as reference. TGA indicated that the decomposition in the Gum Arabic onsets at 215°C with 97% weight loss up to 700°C , while decomposition in the GA-g-3,3-dimethyl acrylic acid onsets at 180°C and 90% weight loss up to 700°C for GA-g-3,3-dimethyl acrylic acid. It was observed that the weight loss was slower in the case of the graft copolymer indicating that the graft copolymer are more thermally stable than the GA.

Table 1. Thermogravimetric data obtained during heating rate at $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere of GA and GA-g-3,3-dimethyl acrylic acid.

Sample	Number of stages	Temperature range ($^\circ\text{C}$)	%Weight loss
GA	1	50-215	9
	2	215-327	70
	3	327-413	7
	4	413-700	14
GA-g-3,3-dimethyl acrylic acid	1	50-180	8
	2	180-700	82

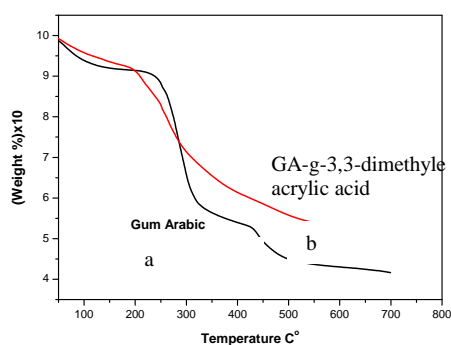


Figure 9-a,b. TGA curves of a) Gum Arabic before grafting and (b) GA-g- 3,3-dimethyl acrylic acid

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