

Diode Laser (532 nm) Induced Grafting of Polyacrylamide onto Gum Arabic

Nafie A. Almuslet^{1*}, Elfatih Ahmed Hassan², Al Sayed Abd-El-Magied Al-Sherbini³ and Mohamed Gusm Alla Muhgoub⁴

¹Institute of Laser, Sudan University of Science and Technology, Khartoum, Republic of Sudan

²Faculty of Science, Sudan University of Science and Technology, Khartoum, Republic of Sudan

³National Institute of Laser Enhanced Sciences, Cairo University, Cairo, Egypt

⁴Faculty of Education, Alzaiem Alazhari University, Khartoum, Republic of Sudan

*Corresponding author: mnmfa2008@yahoo.com

Abstract: Initiation of graft copolymerisation of acrylamide (AAM) on Gum Arabic (GA, *Acacia senegal*) using diode laser (532 nm) was investigated. The results showed that the optimum conditions to achieve efficient graft copolymerisation were: 60 min laser irradiation time and 0.5 gm of GA, 0.142 gm of acrylamide (monomer). The percentage of graft efficiency and percentage of graft yield were 27.40% and 97.40%, respectively. The graft copolymers were characterised using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscope (SEM) which proved a successful production of GA-g-Acrylamide (GA-g-AAM). The results proved that copolymerisation by laser can be considered as a new, effective and clean method for producing GA-g-AAM.

Keywords: polymerisation by laser, graft copolymerisation, laser in photochemistry, laser spectroscopy

1. INTRODUCTION

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

GA is an exudate collected from the stems and branches of *Acacia senegal* and other related African species of *Acacia*. GA is a natural polymer consists mainly of high molecular weight polysaccharides and contains high concentrations of calcium, magnesium and potassium salts, which yield arabinose, galactose, rhamnose and glucuronic acid following hydrolysis. 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 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⁻¹) 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.² 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.³ 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.⁴ Although the structure of the complex has not been fully resolved, it is possible to reconcile the two models. 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.⁵

At present, GA is generally considered safe,⁶ and is widely used as stabiliser, thickening agent and hydrocolloid emulsifier. It is mostly used in food industry, but other sectors such as textile, pottery, lithography, cosmetics and pharmaceutical industries also make use of it.⁷ Several researchers are also studying the application of GA in the development of controlled drug delivery systems,⁸ and carriers for the microencapsulation of oils and other bioactive molecules.^{9,10} 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 stabilisation of nanostructures. As it is a highly branched polysaccharide with high contents of galactose, it has been proven 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,^{11,12} gold nanoparticles,¹³ carbon nanotubes¹⁴ and quantum dot nanocolloids.¹⁵

For the last few decades, chemical modification of GA by graft copolymerisation of vinyl monomers onto it has been a subject of academic as well as industrial interest. Various initiating systems are employed through graft copolymerisation of different monomers onto GA, e.g., Ceric Ammonium Nitrate (CAN), persulfate, microwave and radiation, etc. Less attention has been paid to the grafting of GA by laser. The GA used in graft copolymerisation usually need to be heated in all cases.

In this study, diode laser with wavelength of 532 nm and output power of 200 mW was used to initiate graft copolymerisation of acrylamide onto GA. Different investigations were done to ensure the success of the process.

2. EXPERIMENTAL

2.1 Materials

The GA (*Acacia senegal*) used in this study was obtained from Arabic Gum Company Ltd., Sudan, in spray-dried Mw 1.64×10^5 . Other materials:

- Acrylamide, MP 83° to 85°, assay > 98.5%, MW 71.0, puriss.
- CAN, MW 548; nitric acid, density about 1.42 g mL⁻¹ (Molar Solution); and ethanol, assay > 99.8%, density about 0.790 g mL⁻¹, all were supplied from purum (Fluka Co.).

2.2 Equipment

The equipments used in this study were:

- Diode laser with wavelength 532 nm and power 200 mW, supplied from Hotdiodelaser (USA).
- Fourier transform infrared spectrometer (FTIR), model Perkin Elmer 2000 FT-IR system (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.
- 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 CuK α -radiation at λ 1.54056Å. The relative intensity was recorded in the scattering range (2 θ) of 4–60°.
- Scanning electron microscope (SEM), model 840 Å (JEOL, Japan).
- Thermogravimetric analysis system (TGA), (Shimadzu, Japan) at a heating rate of 10°C min⁻¹.

2.3 Methods

2.3.1 Graft copolymerisation with Cerium IV Ammonium Nitrate (CAN)

The graft copolymerisation of acrylamide onto GA was carried out under different reaction conditions and different concentrations of the monomer to

obtain the optimum conditions of graft copolymerisation. In this study, the graft copolymerisation method was done as follows:

0.5 gram of GA was dissolved in 75 mL of double distilled water and was magnetically stirred under nitrogen for 5 min. This was followed by the addition of required amount of CAN in molar nitric acid with continuous stirring for 15 min to facilitate the formation of free radical sites on the GA chain. A drop wise addition of acrylamide was later performed. The total volume was completed to 100 ml by distilled water. Then the polymerisation process was preceded at 30°C for 3 hr. After the 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.

2.3.2 Laser induced graft copolymerisation

For this case, the method was done as follows:

0.5 gram of GA was dissolved in 75 mL of distilled water, and then it was magnetically stirred under nitrogen for 5 min. Diode laser was used, as initiator, to irradiate the sample for 60 min. The acrylamide (monomer), with concentration of 0.02 mol dm^{-3} , was added. The total volume was completed to 100 ml by distilled water. Then the polymerisation process was preceded at 30°C for 3 hr. The mixture was allowed to cool, and then the solution was washed with water and ethanol repeatedly to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The final product was dried to a constant weight and its percentage of grafting efficiency (%GE) and percentage of grafting yield (%GY) were deduced according to the following equations:¹⁶

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

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

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

3. RESULTS AND DISCUSSION

Graft copolymerisation with CAN was carried out at different concentrations of GA, different monomer concentrations at different temperatures and the time required to complete the reaction in order to obtain the optimum conditions for graft copolymerisation. The deduced optimum conditions were 0.5 gm of GA, 0.142 gm of acrylamide monomer at 30°C and the time

required to complete the reaction was 3 hr. The percentage of graft yield at the optimum conditions was 97% and the percentage of graft efficiency was 27%, as shown in Figure 1.

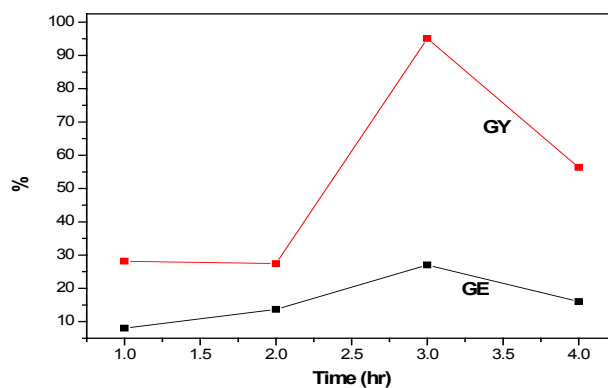


Figure 1: Effect of reaction time on %GE and %GY of GA-g-Acrylamide (GA-g-AAM) [Acrylamide = $0.020 \text{ mole dm}^{-3}$, CAN = 0.91×10^{-3} in 100 mL solution].

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 polyacrylamide in the monomer. The effect of exposure time of diode laser on percentage of graft efficiency and percentage of graft yield of GA-g-AAM was studied and illustrated in Figure 2.

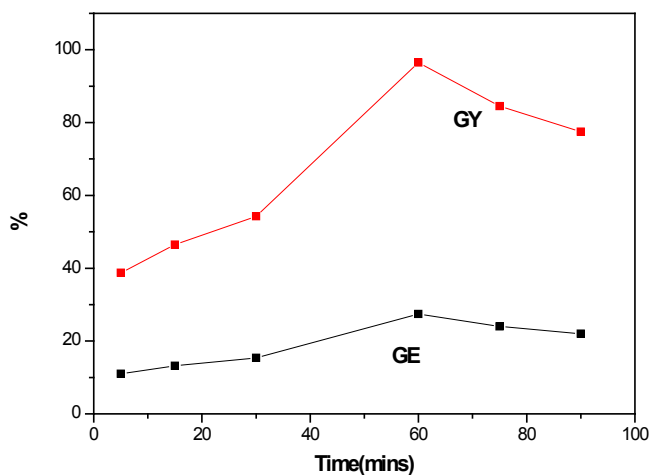


Figure 2: Effect of diode laser exposure time on %GE and %GY of GA-g-AAM (Acrylamide = $0.020 \text{ mole dm}^{-3}$, in 100 mL solution, time 3 hr and temperature 30°C).

The graph is characterised by initial increases in percentage of graft yield and percentage of graft efficiency with exposure time of the laser up to a period of 60 min. With increasing irradiation time, the percentages of graft efficiency and graft yield decreased. The decrease in these percentages after 60 min may be rationalised by partial hydrolysis and dissolution of the grafted polymer chains. It is of interest to illustrate that the percentage of graft efficiency and percentage of graft yield in case of diode laser induced graft copolymerisation were 27.40% and 97.40%, respectively.

Employing laser was an efficient method for initiating graft copolymerisation of GA. Radiation-induced graft copolymerisation has been found to possess potential to simplify the whole treatment process, leave no detrimental residue and reduce the cost of production. It also has the ability to initiate polymerisation in a wide range of temperatures including low region in various states of monomers such as in bulk, solution and emulsion, and even at solid state. Moreover, it offers a unique way to combine two highly incompatible polymers and imparts new properties to the obtained graft copolymers. The versatile nature of this technique is attributed to the ability to control the degree of grafting by proper selection of irradiation conditions.

3.1 FTIR of GA-g-Acrylamide (GA-g-AAm)

As maintained above, the evidence of grafting has been obtained during the graft copolymerisation of different ratios of acrylamide 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 3 presents the FTIR spectra of GA, acrylamide and GA-grafted AA. The figure shows the main vibration bands of unmodified GA, acrylamide and GA-g-AAm, respectively. The GA 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. In case of acrylamide, the recorded spectrum in the same regions indicated the bands at $3359, 3187\text{ cm}^{-1}$ that are ascribed to the antisymmetric and symmetric N–H stretching, respectively.

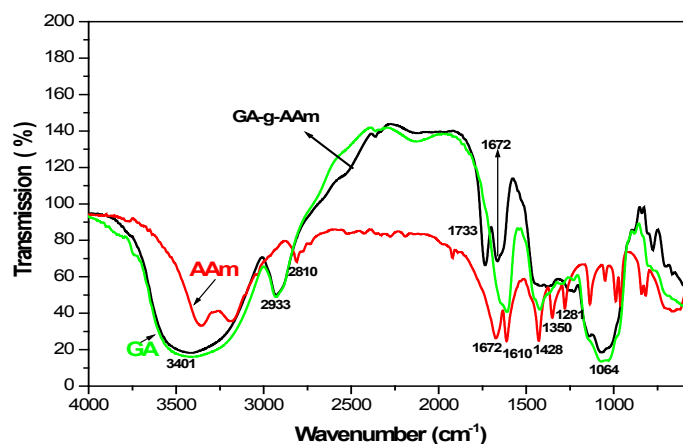


Figure 3: FTIR spectra of GA, AAm and GA-g-AAm in the range from 4000 to 500 cm^{-1} .

In addition, the bands at 3035 and 2812 cm^{-1} are attributed to the symmetric stretching of C-H_2 and vibration of stretching $\nu_{\text{C-H}}$. When the GA was grafted by acrylamide the FTIR spectrum of the grafted copolymerised product showed the same absorption bands as in case of GA within the region 4000–2750 cm^{-1} . It is of interest to illustrate that a new shoulder is observed at 2533 cm^{-1} in case of GA-g-AAm which existed for AAm at 2810 cm^{-1} and disappeared when AAm was grafted in GA. This new shoulder may be due to the vibrational symmetric stretching of CH_2 and vibrational stretching of CH , suggesting the existence of grafting.

Within the range of 2000–1500 cm^{-1} , the FTIR spectrum of GA showed strong peak at 1610 cm^{-1} which is attributed to the COO -asymmetric stretching. In case of acrylamide, the two peaks at 1672 cm^{-1} and 1610 cm^{-1} are due to the $\nu_{\text{C=O}}$, the C=C stretching and in plan bending of N-H_2 , C-H_2 . In the same region, the spectrum of GA-g-AAm, showed a shift of the position of the absorption band from 1610 cm^{-1} for GA to 1672 cm^{-1} . In case of GA-g-AAm, another extra new band at 1733 cm^{-1} appeared, also suggesting the existence of grafting. The peaks at 1733, 1672 and 1610 cm^{-1} are assigned to $\nu_{\text{C=O}}$, $\nu_{\text{C-O}}$ and N-H_2 deformation ($\delta \text{ N-H}_2$). The FTIR spectrum of GA showed a weak absorption band at 1420 cm^{-1} assigned to COO - symmetric stretching, while for AAm the peak observed at 1428 cm^{-1} is for $\delta \text{ sci} (\text{CH}_2)$. In the same region, the intensity of the two peaks decreased in the case of GA-g-AAm. The same results were obtained for the AAm which has two peaks at 1350 and 1281 cm^{-1} that disappear in GA-g-AAm. The strong peaks at 1200–900 cm^{-1} are the finger print of carbohydrates. These peaks are observed in the case of GA and GA-g-AAm, while disappeared for AAm which has four absorption peaks at 1138, 1048, 988

and 961 cm^{-1} due to the rocking of N-H₂, C-H₂, in plan bending of C-H and (wagging trans of CH=CH, wagging of CH₂), respectively.

Within the range of $900\text{--}500\text{ cm}^{-1}$, the FTIR spectrum of acrylamide showed absorption bands at $840, 817\text{ cm}^{-1}$ and other bands observed from $700\text{--}500\text{ cm}^{-1}$. These peaks are assigned to ν (C-C), τ (torsion) (NCC) + τ (CCC), ρ (NH₂) + ρ (CH₂) and ρ (NH₂) + ρ (CH₂), respectively. In the same domain, the GA showed weak peaks assigned to CCO, COC, symmetrical and asymmetrical ring breathing vibration. After graft copolymerisation, the spectrum showed that the peak at 840 cm^{-1} for (ν (C-C)) decreased in case of acrylamide while the other peak at 817 cm^{-1} disappeared. On the other side, there are two shoulders observed at 882 cm^{-1} and 806 cm^{-1} which became weaker in the grafted GA rather than GA, respectively. It is also observed that there is an increase in the optical density of all other shoulders from 777 cm^{-1} to 601 cm^{-1} for grafted GA. This indicates that the grafting of Gum Arabic with acrylamide had taken place which showed the same shoulder in the same domain.

3.2 X-ray Diffraction (XRD) of GA and GA-g-AAm

Figure 4 illustrates the powder X-ray diffractograms obtained for natural GA, before and after grafting, respectively. The XRD pattern shows the amorphous nature of GA. From spectrum (a), 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 copolymerisation of GA with acrylamide, the peak was shifted considerably to $2\theta = 20.4^\circ$ which has the average grain length estimated to $d\text{-space} = 4.818\text{ \AA}$. On the other side, spectrum (b) shows that the grafting decreases the intensity of the corresponding peak. The graft copolymerised sample become almost amorphous. The grafting of acrylamide 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 resulted the formation of amorphous copolymer.

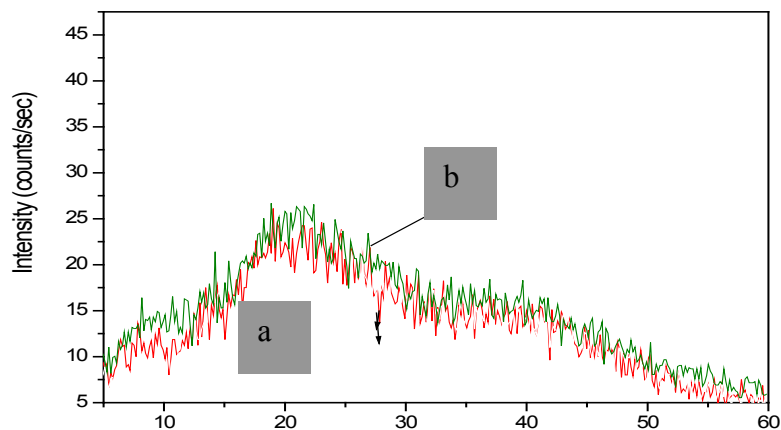


Figure 4: XRD of (a) GA (b) GA-g-20 AAm.

3.3 SEM of GA and GA-g-AAm

Morphological examination of the fine powder of GA and grafted copolymerised 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-AAm was studied by SEM and compared with the GA. The exterior surface of the GA-g-AAm appears as irregular rocky surface and clearly different from that of the parent GA, which has spherical shape with many dents on the surface. The surface evidence supports the grafting of AAm onto the GA as shown in Figure 5 (a and b).

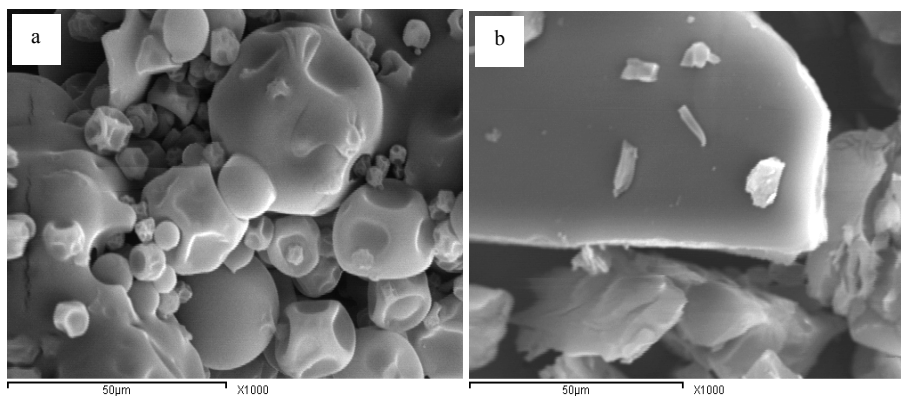


Figure 5: Typical SEM images of (a) GA before grafting, and (b) GA-g-AAm.

4. CONCLUSION

The graft copolymers characterisation has resulted in a successful production of GA-g-AAm. This work proved that copolymerisation by laser can be considered as new, effective and clean method for producing GA-g-AAm.

5. ACKNOWLEDGEMENT

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