

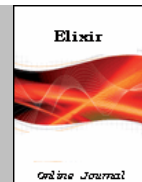


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Graft copolymerization of acrylamide onto gum karaya using diode laser (532nm)

Nafie A. AlMuslet⁽¹⁾, Elfatih Ahmed Hassan⁽²⁾, Al Sayed Abd-El-Magied Al-Sherbini⁽³⁾, Mohamed Gusm Alla Muhgoub⁽⁴⁾.¹Institute of Laser, Sudan University of Science & Technology, Khartoum / Republic of Sudan,²Faculty of Science, Sudan University of Science & Technology, Khartoum / Republic of Sudan.³National Institute of Laser Enhanced Sciences (NILES), Cairo University, Cairo / Egypt,⁴Faculty of Education, Alzaiem Alazhari University, Khartoum / Republic of Sudan.

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ABSTRACT

Graft copolymerization of acrylamide (AAm) on Gum Karaya GK using diode laser (532 nm) was investigated. The results showed that, the optimum conditions to achieve efficient graft copolymerization were: 60 minutes laser irradiation time and 0.5 gm of GK, 0.142 gm of acrylamide (monomer). The percentage of graft efficiency and percentage of graft yield were 28.00%, and 98.59%, respectively. The graft copolymers were characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Thermogravimetric analysis (TGA) and Scanning Electron Microscope (SEM) which proved a successful production of GK-g-AAm. Thus, Laser irradiation was found to be effective and clean method for producing GK-g-AAm.

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Introduction

Gum Karaya:

Scientific Name(s): *Sterculia urens* Roxb. Family: Sterculiaceae. The gum also may be obtained from *S. villosa*, *S. tragacantha*, or other species of *Sterculia* [1].

Common Name(s): Karaya, sterculia. In Sudan, and elsewhere in Africa, gum karaya can be obtained from *S. setigera*. The exudates from these three species are very similar in chemical composition and physico-chemical characteristics. Accordingly, in terms of current legal definitions of identity and trade specifications, exudates from any *Sterculia*, or admixtures, can be offered for sale. *Sterculia setigera* is a multi-purpose savanna tree which spreads naturally in central and southern Sudan. The species is the main source of the internationally accepted, Gum Karaya in Sudan [2,3,4,5]. Traditionally, India is the largest producer and exporter of karaya gum [6]. Increasing amounts are exported by African countries. Currently the gum is used in a variety of products, including cosmetics, hair sprays, and lotions, to provide bulk [7].

Gum Karaya is a complex, partially acetylated polysaccharide obtained as a calcium and magnesium salt. The polysaccharide component of gum karaya has a high molecular weight and is composed of galacturonic acid, beta-D-galactose, glucuronic acid, L-rhamnose, and other residues [1,2,3]. The quality of gum karaya depends on the thoroughness of impurity removal. Food-grade gum is usually a white to pinkish gray powder with a slight vinegar odor [2]. Pharmaceutical grades of gum karaya may be almost clear or translucent [3].

Gum Karaya is not digested or absorbed systemically. It is essentially inert and is not associated with any pharmacologic activity. Gum Karaya has a number of applications in the food industry. Medicinally, gum karaya is an effective bulk laxative as gum particles absorb water and swell from 60 to 100 times their original volume [6]. The mechanism of action is an

increase in the volume of the gut contents. Gum Karaya should be taken with plenty of fluid and it may take a few days for effects to be noticeable. It also has been used as an adhesive for dental fixtures and ostomy equipment, and as a base for salicylic acid patches [8,9]. Some preliminary studies suggest that gums may normalize blood sugar and plasma lipid levels [10], but this has not been thoroughly investigated. The use of gum karaya as a carrier for drugs with differing solubilities in aqueous medium has been investigated [11,12].

Experimental part:

Materials:

Gum Karaya collected from South Kordfan region, Sudan during season 2007 and was used after cleaning from park, leaves and extraneous materials without further purification. Also other materials were used such as:

Acrylamide, 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)- Diode laser with wavelength of 532 nm and Power of 200 mW, supplied from (USA).

(2) -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} .

(3) - X-ray Diffraction system attached with liquid nitrogen cooled detector, model *Brukur 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 λ 1.54056Å. The relative intensity was recorded in the scattering range (2 θ) of 4–60°.

(4) - Scanning Electron Microscope (SEM), supplied from *JEOL*

Tele:

E-mail addresses: mnmfa2008@yahoo.com

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(Japan) model 840 A°,

(5) - Thermogravimetric analysis system (TGA) supplied from Shimadzu (Japan) at a heating rate of 10°C/min.

Methods:

(1) -Graft Copolymerization with Cerium IV ammonium nitrate (CAN):

The graft copolymerization of acrylamide onto Gum Karaya 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 Karaya 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 Karaya chain followed by drop wise addition of acrylamide.

The total volume was completed to 100 mL by distilled water. Then the polymerization process was preceded at 30 ° C for 3 hours. 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.

Laser Induced Graft Copolymerization:

In this case the method was done as follows:

0.5 gram of Gum Karaya was dissolved in 75 mL of distilled water, and then it was magnetically stirred under nitrogen for 5 minutes. Diode laser was used, as initiator, to irradiate the sample for 60 minutes. 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 polymerization process was preceded at 30 ° C for 3 hours.

The mixture was allowed to cool then 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 [13]:

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

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

where W₁, W₂ and W₃ denote, the weights of the natural polymer, graft copolymer and monomer, respectively.

Results and Discussion:

First of all graft copolymerization with Cerium IV ammonium nitrate (CAN) was carried out at different concentrations of GK, different monomer concentrations at different temperatures and the time required to complete the reaction in order to obtain the optimum conditions for graft copolymerization.

The deduced optimum conditions were 0.5 gm of GK, 0.142 gm of acrylamide (monomer) at 30°C and the time required to complete the reaction was 3 hrs.

The percentage of graft yield at the optimum conditions was 97% and the percentage of graft efficiency was 27%, as shown in fig.(1).

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.

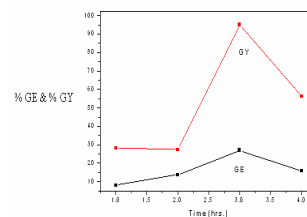


Figure (1) Effect of reaction time on % graft efficiency and % graft yield of GK-g-AAm (Acrylamide =0.020 mole dm⁻³, CAN=0.91x10⁻³ in 100 ml solution.

The effect of exposure time of diode laser on percentage of graft efficiency and percentage of graft yield of GK-g-AAm was studied and illustrated in figure (2).

The graph is characterized 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 minutes. With increasing the irradiation time the percentage of graft efficiency and percentage of graft yield decreases. The decrease in percentage of graft yield and percentage of graft efficiency after 60 minutes may be rationalized 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 copolymerization were 28.00% and 98.59%, respectively. Employing laser was an efficient method for initiating graft copolymerization of Gum Karaya.

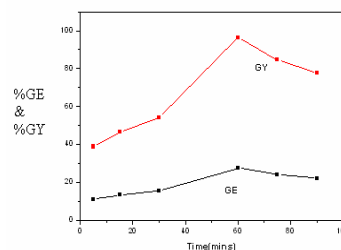


Fig. (2) Effect of diode laser exposure time on % GE and % GY of GK-g-AAm (Acrylamide =0.020 mole dm⁻³, in 100 ml solution, time 3 hour and temp. 30 °C).

FTIR of GK-g-Acrylamide:

As maintained above the evidence of grafting has been obtained during the graft copolymerization of different ratios of acrylamide onto GK, 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 of Gum Karaya, acrylamide and Gum Karaya grafted AAm. The figure shows the main vibration bands of unmodified Gum Karaya, acrylamide and GK-g-AAm, respectively. The Gum Karaya showed a broad absorption band at 3420 cm⁻¹. This band is a characteristic of the glucosidic ring and might due to the stretching vibration of O-H, a small peak at 2933 cm⁻¹, attributed to the C-H stretching vibration. In case of acrylamide the recorded infrared spectra in the same regions shows bands at 3359, 3187 cm⁻¹ ascribed to the antisymmetric and symmetric N-H stretching, respectively. In addition the bands at 3035 and 2812cm⁻¹ were attributed to the symmetric stretching of C-H₂ and vibration of stretching ν_{C-H}. In case of acrylamide, the recorded spectrum in the same regions indicated the bands at 3359, 3187 cm⁻¹ that are ascribed to the antisymmetric and symmetric N-H stretching, respectively.

In addition, the bands at 3035 and 2812cm⁻¹ are attributed to

the symmetric stretching of C-H₂ and vibration of stretching ν_{C-H} . When Gum Karaya was grafted by acrylamide the FTIR spectra of the grafted copolymerized product showed the same absorption band as in case of Gum Karaya. It is of interest that new peaks are observed at 2497 cm⁻¹ and 2336 cm⁻¹ in case of GK-g-AAm. These new peaks may be due to the vibrational symmetric stretching of CH₂ and vibrational stretching CH, respectively suggesting the existence of grafting. In the region between 2000-1500 cm⁻¹, the FTIR of GK showed two peaks at 1731 cm⁻¹ and 1610 cm⁻¹ which attributed to the C=O stretching and C=C stretching respectively.

In case of acrylamide the peaks between 1672 cm⁻¹ 1610 cm⁻¹ are due to the $\nu_{C=O}$, the C=C stretching and in plan bending of (N-H₂, C-H₂). In the same region the spectra of GK-g-AAm, showed shift of the position of the absorption band from 1610 cm⁻¹ for GK to 1634 cm⁻¹ and from 1731 cm⁻¹ for GK to 1740 cm⁻¹. In case of GK-g-AAm this shift also evidence of grafting. The peaks at 1740 cm⁻¹ and 1634 cm⁻¹ are assigned to $\nu_{C=O}$, ν_{C-O} and N-H₂ deformation (δ N-H₂) respectively.

In the domain of 1500-500 cm⁻¹, the FTIR of Gum Karaya showed peak at 1521 cm⁻¹ due to C=C stretch and a weak band at 1432 cm⁻¹ assigned to symmetric CO₂ stretch while for AAam the peak observed at 1428 cm⁻¹ is due to C-N stretching. In the same region, the peaks at (1521, 1423 cm⁻¹) were disappeared in case of GK-g-AAm.

This might be due to the grafting. Acrylamide shows two peaks at 1350 cm⁻¹ and 1281 cm⁻¹ while GK-g-AAm has peaks at 1323 cm⁻¹ and 1285 cm⁻¹ assigned to OH bending vibration and C-O antisymmetric and symmetric stretching vibration, respectively. The strong peaks from 1200-900 cm⁻¹ are the finger print of carbohydrates.

These peaks are observed in case of GK and GK-g-AAm, while disappeared for AAam 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 900-500 cm⁻¹, the FTIR of acrylamide showed absorption bands at 840, 817 cm⁻¹ and other bands observed from 700-500 cm⁻¹.

These peaks are assigned to ν (C-C), r (torsion) (NCC) + r (CCC), ρ (bending) (NH₂) + ρ (CH₂ and ρ (NH₂) + ρ (CH₂), respectively. In the same domain the Gum Karaya showed weak peaks assigned to CCO, COC, symmetrical and asymmetrical ring breathing vibration. After graft copolymerization the product showed that the peak at 882 cm⁻¹, 853 cm⁻¹ and 817 cm⁻¹ (ν (C-C)) decrease in case of acrylamide while the other peak at 817 cm⁻¹ is not observed. It is also observed that there are three new peaks at 670 cm⁻¹ to 611 cm⁻¹ and 580 cm⁻¹ in case of grafted Gum Karaya which are not existed in case of both AAam and GK. This indicated that Gum Karaya was grafted with acrylamide.

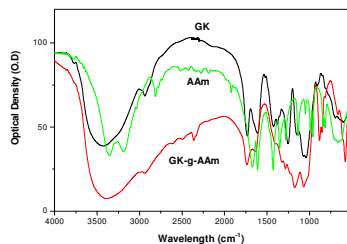


Figure (3) FTIR spectra of GK, Acrylamide, and GK-g-Acrylamide in the range from 4000 to 500 cm⁻¹.

X-ray Diffraction (XRD) of GK and Gum Karaya-g-Acrylamide:

Fig. (4-a,b) illustrated the powder X-ray diffractograms obtained for natural GK, before and after grafting, respectively. The XRD pattern shows the amorphous nature of GK. From figure (4a), the maximum intensity is at $2\theta = 20^\circ$ which well agreed with values reported in literatures. The observed peak corresponds to $2\theta = 19.895^\circ$, has the average grain length estimated to d -space = 4.4375\AA . The XRD pattern provides an interesting feature of intensity distribution. After carrying out the graft copolymerization of GK by acrylamide, the peak of the distribution was shifted considerably to $2\theta = 20.79^\circ$ which has the average grain length estimated to d -space = 4.267\AA in comparison to the Gum Karaya. On the other hand fig.(4b) shows that the grafting decreases the intensity of the corresponding peak. The graft copolymer becomes almost amorphous. The grafting of acrylamide is taken place randomly along the GK chain, giving rise to a random copolymer. This will efficiently destroyed the regularity of the packing of the original GK chains, which results in the formation of amorphous copolymer.

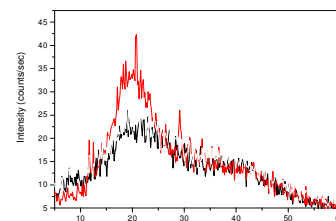


Fig (4-a,b) XRD of (a) Gum Karaya Gum and (b) Karaya-g-Acrylamide.

Scanning Electron Microscope (SEM) of GK and GK-g-Acrylamide:

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 GK-g-AAm studied by SEM and compared with the GK. The exterior surface of the GK-g-AAm appears as heterogeneous rocky surface and clearly different from that of the parent GK, which has rocky shape of smooth surface with different sizes. Hence, the surface evidence supports the grafting of AAam onto the GK, as shown in Fig. (5-a,b).

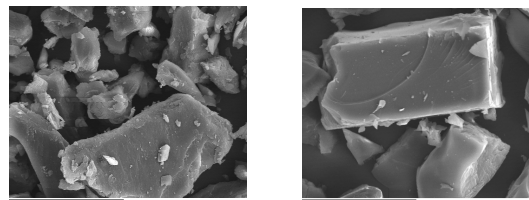


Figure (5-a,b) Typical SEM images of (a) Gum Karaya before grafting and (b) GK-g-AAm.

Thermogravimetric Analysis (TGA):

(1) - Gum Karaya-g-Acrylamide:

In this study TGA was done on the dried samples in air with a heating rate of 10 °C/min. Figure (6-a,b) and table (1) illustrate the details of thermal behavior according to the primary thermograms and derivative thermograms for Gum Karaya and Gum Karaya-g-Acrylamide. The samples showed

first a small weight loss (15%) up to 250°C and (9%) up to 249°C for GK and GK-g-AAm, 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 Karaya exhibited three stages, the first stage is attributed to desorption of moisture as hydrogen bound water to the gum structure while the second and third stages of TGA curve are probably due to molecular degradation and decomposition reactions of GK. It was observed that the weight loss was slower in the case of the graft copolymer indicating that the graft copolymer is more thermally stable than the GK.

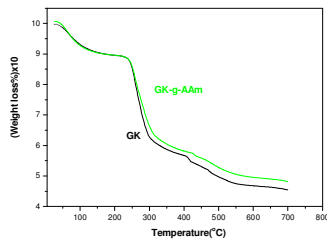


Figure (6-a,b) TGA curves of a) Gum Karaya before grafting and (b) GK-g-AAm.

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Table (1) Thermogravimetric data obtained during heating rate at 10 °C/min under nitrogen atmosphere of GK and GK-g-AAm.

Sample	Number of stage	Temperature range (°C)	Weight loss (%)
GK	1	50-250	15
	2	250-400	65
	3	400-700	20
GK-g-AAm	1	50-249	9
	2	300-700	81