

Graft Copolymerization of Acrylamide onto Anogeissus Leiocarpus Gum Using Ceric Ammonium Nitrate

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Abstract: Graft copolymerization of acrylamide (AAm) on Anogeissus leiocarpus Gum (ALG) using Ceric ammonium nitrate was investigated. The results showed that, the optimum conditions to achieve efficient graft copolymerization were: 0.5 gm of ALG, 0.142 gm of acrylamide and 0.05 gm ceric ammonium nitrate (CAN). The percentage of graft efficiency and percentage of graft yield were (26%) and (75.5%), respectively. The graft copolymers were characterized using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Thermogravimetric analysis (TGA) which proved a successful production of AL-g-AAm.

Key words: Anogeissus leiocarpus gum • Graft copolymerization • CAN • X- ray diffraction

INTRODUCTION

Gums are complex mixtures of polysaccharides and glycoproteins. It was historically the source of the sugars arabinose, galactose and uronic acid, which are isolated from it and are named after it [1]. Gums are used primarily in the food industry as a stabilizer. Gum is a key ingredient in traditional lithography and is used in printing, paint production, glue, cosmetics and various industrial applications, including viscosity control in inks and in textile industries, although less expensive materials compete with it for many of these roles [1]. Plant gums are harvested from wild trees throughout the Sahel from Senegal to Somalia, although it has been historically cultivated in Arabia and West Asia. While gum is now produced mostly throughout the African Sahel, it is still harvested and used to make a chilled, sweetened and flavored gelato - like dessert [1]. *Anogeissus leiocarpus* is a tall evergreen tree native to savannas of Tropical Africa [2]. It is sole West African species of the genus *Anogeissus*, a genus otherwise distributed from tropical central and east Africa through tropical Southeast Asia, [3] in Sudan it is found in southern Kordofan (Nuba mountain) and southern Darfour [4]. *Anogeissus leiocarpa* germinates in the new soils produced by seasonal wetlands and grows at the edges of the rainforest, in the savanna and along riverbanks forming gallery forests. The tree flowers in the rainy season, from June to October. The seeds are dispersed by ants [5].

The natural polysaccharide polymers, *i.e.* *Anogeissus leiocarpus* gum, are been reported for their application in pharmaceutical and biomedical fields for the controlled release of drugs [5].

They do gain certain properties over synthetic polymers, *e.g.* nontoxic, biodegradable, less expensive and without stinting available compare to the synthetic polymer [6]. Modification of polymer by addition, subtraction, self-reaction, or cross reaction with other entities have the capability of generating polymers with properties that are enable to create novel pharmaceutical and medical products [7]. Because it possessed very low hydration capacity, higher erosion property and susceptibility to microbial attack, it was meant to be grafted with different vinyl monomers with employing initiators [8].

Graft copolymer is a branched copolymer in which the backbone and the branches are of different monomers. They have been widely prepared by different techniques or reactions.

Graft copolymerization is considered to be one of the routes to create natural and synthetic polymers [9, 10]. The modification of natural polymers such as starch [9, 11, 12], cellulose [13, 14], chitosan [15, 16, 17], Gums like *Anogeissus leiocarpus* gum, arabic gum and Gum karaya gum etc.... have been finding a large interest in academic research and industry [18, 19], not only because of their abundance in nature and their low cost, but also because of the biodegradability of their polysaccharide portion, so

graft copolymers of these natural polymers find large application in industry, agriculture, medical treatment, sanitation, dehumidification, dehydration, water preservation, water absorption and in drug sustained release. As a result they have been accepted as thickeners [20], sizing agents [21], super absorbent in diapers and sanitary napkin [22], as soil stabilizers [23] and in biodegradable thermoplastics [24].

The use of laser to initiate polymerization of vinyl monomers has attracted attention and several reports have been published. This is mainly due to capability of laser to be tuned to a specific wavelength, therefore exciting a particular band [25, 26].

MATERIALS AND METHODS

Anogeissus leiocarpus gum were obtained from different location in Sudan, the gum samples were collected from gum belt namely from Abojebiha and Elfula, the gum samples were cleaned by hands to remove foreign particles. The samples were then ground using mortar and piston, sieved through sieve 250 μm and kept in plastic container for further analysis.

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:

- 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} .
- X-ray Diffraction system attached with liquid nitrogen cooled detector, model *Bruker D 8 Advance* (Germany),
- Thermogravimetric analysis system (TGA) supplied from *Shimadzu* (Japan) at a heating rate of 10°C/min.

Methods: Graft Copolymerization with Cerium IV ammonium nitrate (CAN):

The graft copolymerization of acrylamide onto Anogeissus leiocarpus gum 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 Anogeissus leiocarpus gum was dissolved in 75 mL of distilled water and 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 Anogeissus leiocarpus gum 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 and its percentage of grafting efficiency (%GE) and percentage of grafting yield (%GY) were deduced according to the following equations [27]:

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

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

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

RESULTS AND DISCUSSION

First of all graft copolymerization with Cerium IV ammonium nitrate (CAN) was carried out at different concentrations of AL Gum, 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 AL Gum, 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.

FTIR of AL G -g-Acrylamide: As maintained above the evidence of grafting has been obtained during the graft copolymerization of different ratios of acrylamide onto AL G, from the increases in weight of the product of the graft copolymer compared with the original substrate.

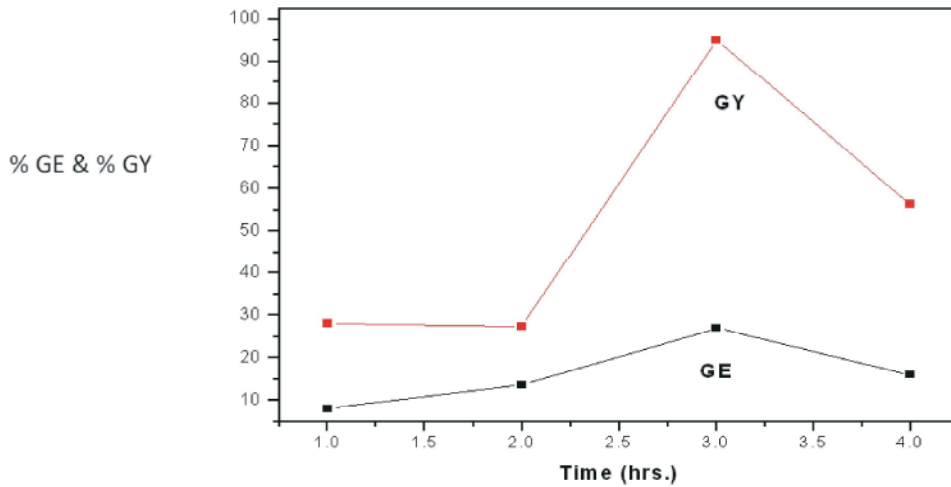


Fig. 1: Effect of reaction time on % graft efficiency and % graft yield of ALG-g-AAm (Acrylamide = 0.020 mole dm⁻³, CAN = 0.91x10⁻³ in 100 ml solution)

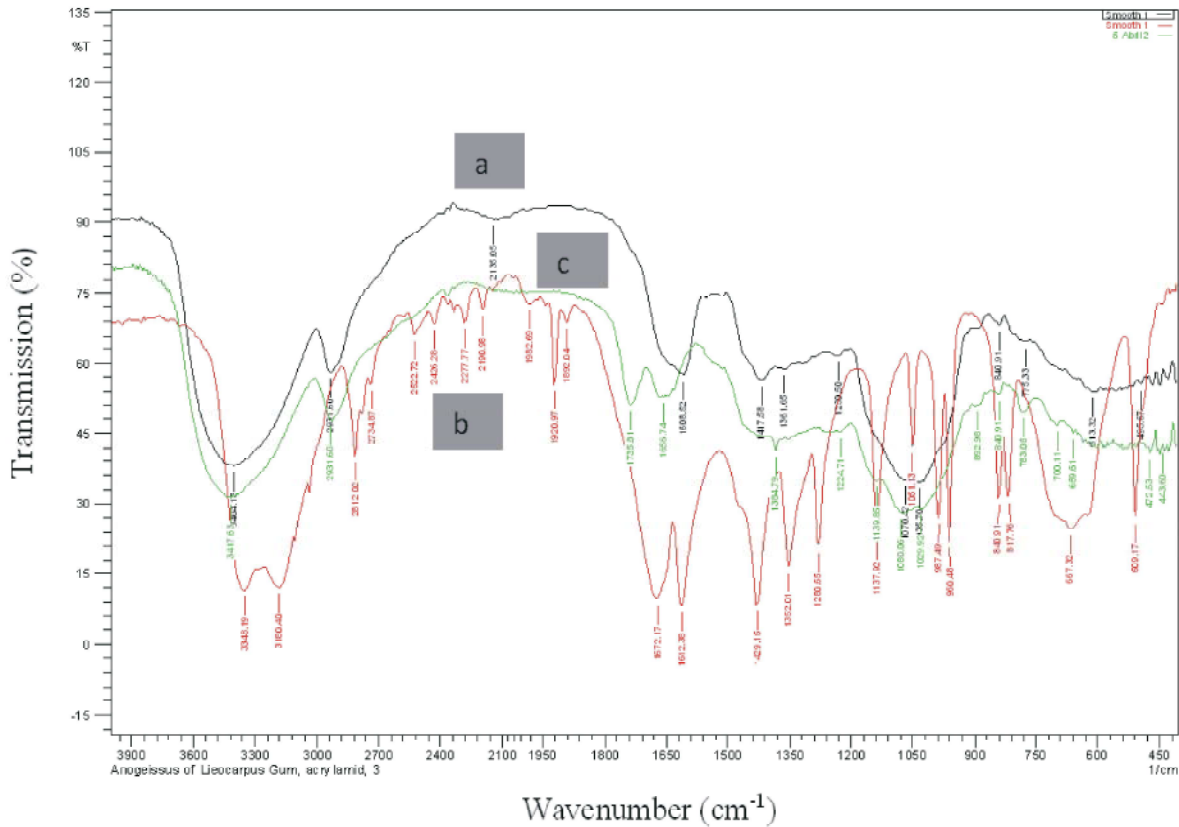


Fig. 2: FTIR spectra of (a)AL G, (b) Acrylamide, and (c) AL G -g-Acrylamide in the range from 4000 to 500 cm⁻¹

Also the evidence of grafting was observed among the infrared spectra comparison between the substrate and graft copolymer. Figure (2) presents the FTIR of AL G, acrylamide and AL G grafted AAm. The figure shows the main vibration bands of unmodified AL G, acrylamide and AL G -g-AAm, respectively.

The FT-IR spectrum of *Anogeissus leiocarpus* Gum has strong vibrational band located at 3600 - 3000 cm⁻¹ is assigned to the stretching vibrations of the O-H, the other strong vibrational band at 1624 cm⁻¹ is assigned to the stretching vibrations of the C = O bond of carboxylate group associated with the *Anogeissus leiocarpus* Gum

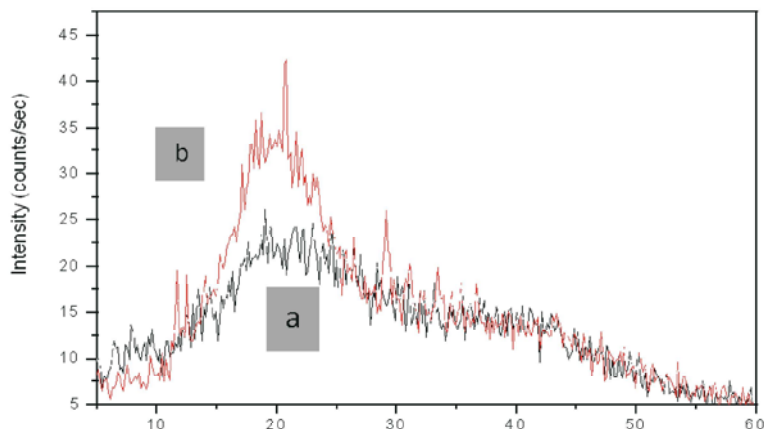


Fig. (3-a, b): XRD of (a) AL G and (b) AL-g-Acrylamide

Table 1: Thermogravimetric data obtained during heating rate at 10°C/min under nitrogen atmosphere of AL G and AL G -g-AAm

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

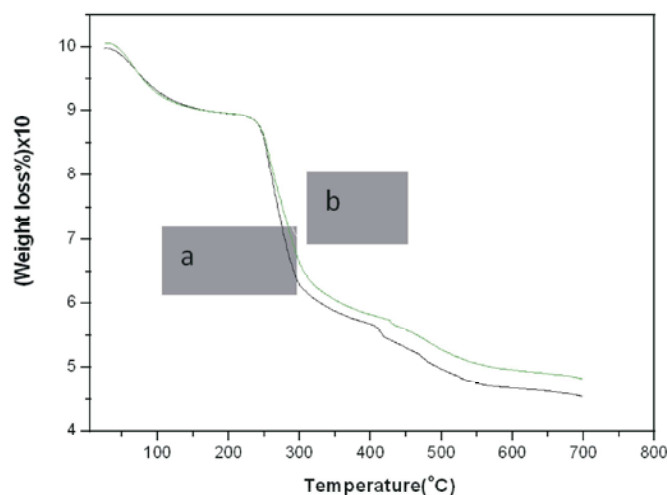


Fig. (4-a,b): TGA curves of a) AL G before grafting and (b) AL G -g- AAm.

molecules, the two vibrational bands at 1066 and 1430 cm^{-1} , with relatively low intensity, are assigned to the stretching vibrations of the C- O bond and the weak vibrational band located at 2930 cm^{-1} is assigned to the stretching vibrations of the C-H bond. The absorption band located at 2309 cm^{-1} , with relatively low intensity, is usually assigned to the CO_2 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 2812 cm^{-1} were attributed to the symmetric stretching of C-H₂ and vibration of stretching $\nu_{\text{C-H}}$. Also FTIR spectrum of acrylamide show peaks between 1672 cm^{-1} -1610 cm^{-1} are due to the $\nu_{\text{C=O}}$, the C=C stretching and in plan bending of (N- H₂, C-H₂).

The graft copolymer of ALG -g- acrylamide spectrum show An absorption peak at 3180.40 cm^{-1} may attributed to stretching C-H sp^2 shifted to lower frequency 2927.74 cm^{-1} C-H sp^3 which have more p character.

Also the absorption bands at 1612.38 cm^{-1} , 987.49 cm^{-1} (near), 960.48 cm^{-1} (near) and 667.32 cm^{-1} (out-of-plane) may attributed to stretching $\text{C}=\text{C}$, those band disappeared on grafted polymer spectrum, may be taken as an evidence that grafting has occurred.

A rocking band appears at 700.11 cm^{-1} for long-chain alkanes of four carbons or more, while the band at 1429.15 cm^{-1} scissoring $\text{C-H } sp^2$ has been disappeared on grafted polymer spectrum. The new most important band at 781.12 cm^{-1} may be attributed to stretching C-O-C which confirms that the grafting is complete.

X-Ray Diffraction (XRD) of AL G and AL G -g-Acrylamide: Fig. (3-a, b) illustrated the powder X-ray diffractograms obtained for natural AL G, before and after grafting, respectively. The XRD pattern shows the amorphous nature of AL G. From Figure (3a), 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 $d\text{-space} = 4.4375\text{ \AA}$. The XRD pattern provides an interesting feature of intensity distribution. After carrying out the graft copolymerization of AL G by acrylamide, the peak of the distribution was shifted considerably to $2\theta = 20.79^\circ$ which has the average grain length estimated to $d\text{-space} = 4.267\text{ \AA}$ in comparison to the AL G. On the other hand Fig. (3b) 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 AL G chain, giving rise to a random copolymer. This will efficiently destroyed the regularity of the packing of the original AL G chains, which results in the formation of amorphous copolymer.

Thermogravimetric Analysis (TGA):

AL G -g-Acrylamide: In this study TGA was done on the dried samples in air with a heating rate of $10^\circ\text{C}/\text{min}$. Figure (4-a, b) and Table (1) illustrate the details of thermal behavior according to the primary thermograms and derivative thermograms for AL G and AL G -g-Acrylamide. The samples showed first a small weight loss (15%) up to 250°C and (9%) up to 249°C for AL G and AL G -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 AL G 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 AL G. 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 ALG.

CONCLUSION

Natural gums are promising biodegradable polymeric materials. Many studies have been carried out in fields including food technology and pharmaceuticals using gums. It is clear that gums have many advantages over synthetic materials. Various applications of gums have been established in the field of pharmaceuticals.

However, there is a need to develop other natural sources as well as with modifying existing natural materials for the formulation of novel drug delivery systems, biotechnological applications and other delivery systems. Therefore, in the years to come, there will be continued interest in natural gums and their modifications aimed at the development of better materials for drug delivery systems.

ACKNOWLEDGMENT

The author would like to express his appreciation to the head department of Chemistry, Faculty of Science, University of Jeddah, for their invaluable assistance and guidance during practical work.

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