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DIODE LASER-INDUCED GUM ARABIC-G-ACRYLIC ACID

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Abstract

Aim of this study is to synthesis Gum Arabic-g-Acrylic acid using laser light as initiator to synthesis clean product that is free from any trace's chemicals substances. Firstly the graft of acrylic acid on Gum Arabic, initiated by (C.A.N), will be study under a nitrogen gas to get reaction conditions such as graft copolymerization temperature, reaction time, and Gum Arabic, monomer, and initiator concentrations. Percentage of graft efficiency (% GE) and percentage of graft yield (% GY) will be collocated. Graft copolymer will be recognized using FTIR Spectroscopy, (TGA) analysis, (XRD) diffraction and (SEM) microscope. The graft will be later used in drug delivery carrier to control cancer in brain and matrices for colon aiming medicine delivery systems. This study focused to new trends and latest developments in this area where laser light was found to be efficient and clean method for synthesis GA-g-Acrylic Acid.

Keywords
Laser Irradiation, Drug Delivery Carrier, Acrylic Acid, Graft Copolymer

1. Introduction

Graft copolymerization is a large molecular at one or more sort of block linked to essential chain as part chain(s) (Athawale & Rathi, 1999).
From figure one backbone poly (A), generally indicate as body of polymer, with branches polymer chain poly (B). So we can say when poly (A) grafting with poly (B), poly (A)-graft-poly (B). Graft copolymerization are making out of graft of vinyl in the fundamental polymer (Mahdavinia, Zohuriaan & Pourjavadi, 2004). Graft copolymerization is a paramount method for adjusting properties of polymers (Nevin, 2016).

Grafting of natural and modified polymer has added combination extra properties of monomers to polymers (Singha, Guleria, & Rana, 2013).

![Image](image.png)

**Figure 1:** General Free Radical Mechanism of Grafting (B) on poly (A)

Gum Arabic 'Hashab', produced by Acacia trees. Gummosis is wound response that results in the exudation of a plastic gummy sealant at the site of cracks in bark. When tree damaged give a larger product of gum. So as we cut and strip the bark from a tree and come to take liquid solution form tree.

Within 3-8 weeks, gums will begin to exclude from the wound. Gum droplets are about 0.75 - 3 inches in diameter, gradually dry and harden on exposure to the atmosphere. A young tree will product 400 - 700 g per year (Stephen, Churms, & Vogt, 1990). GA is a complex has galactopyranose units (Dickinson & E., 2003).

Up-to-date a numbers of initiator systems advanced to initiate graft copolymerization. We used many substances, like CAN, potassium persulfate, and ammonium persulfate, usually, to make a free radical on polymers. Initiating the vinyl monomer onto polysaccharides, (CAN) used as an initiator
extensively investigated therefore the simple mechanism of electron transfer, low activation energy and forming of free radical on the a polymer. Cerium most frequently, in grafting many monomers on cellulose and starch (Athawale & Rathi, 1999; Fernandez, Casinos, & Guzman, 1990).

Many researchers used laser light as initiator (Kesling, & Schollmeyer, 1990; Hoyle, Chang, & Trapp, 1989). Therefore capability of laser to be adjusted to a specific wavelength, therefore exciting a particular band. Decomposition of cyclohexene-1, 4-cyclohexadiene and hexahydro-1, 3, 5-trinitro-1, 3, 5 -triazine molecules excited via a multi photon process by employ of CO₂ transverse electrical discharge in gas at atmospheric pressure (TEA CO₂) laser has been present by Zhao and coworkers (Zhao, Continetti, Ynkuyama, & l,.1989; Zhao, Hinsta & Lee 1988).

Surface modification through etching in the air by CO₂-pulsed laser has also done by (Brannon & Lankari, 1986). The capability of CO₂ - pulsed laser to graft many monomers onto surface of ethylene-propylene rubber to improved water and biocompatibility has been explained (Mirzadeh, Kathah, & Burford, (1993; Mirzadeh, Khorasani, Katbab, Ilurford, Sohcili & Z ., 1994). Ethylene-propylene rubber (EPR) grafts acrylamide (AAm) and 2-hydroxy ethyle methacrylate (HEMA) by CO₂ - pulsed laser (Mirzadeh, Katbab, Khorasani, & Burford 1994).

Last year’s we used a laser as initiator for grafting many monomers such as: 3,3-dimethylene acrylic acid grafted on GA (Nafie AlM., Elfatih A., Al Sayed, & Mohamed M. S., 2010), Gum Karaya –g-acrylamide (Nafie AlM., Elfatih A., Al Sayed, & Mohamed M. S., 2011), graft polyacrylamide onto GA (Nafie AlM., Elfatih A., Al Sayed, & Mohamed M. S., 2012), and 3,3-dimethylene acrylic acid grafting in Gum Karaya (Mohamed G. M. S., Mohamed A., Essam A., & Hayat Elb., 2015).

The use of laser in graft copolymerization importance because laser tuning to particular wavelength, therefore exciting a particular band (Kesling, & Schollmeyer, 1990), Hoyle, Chang & Trapp, 1989).

The objectives of our study:

- Synthesis graft copolymer of GA-g-acrylic acid using laser light as initiator.
- Optimize conditions of graft copolymer.
- Study the variation of %GE and %GY with different reaction parameters.
- Characterize synthesized graft copolymer using various techniques such as:
  - Fourier transforms infrared spectroscopy (FTIR).
  - XRD.
  - Thermogravimetric Analysis (TGA).

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2. Experimental Analysis

2.1 Materials

Gum Arabic (Acacia Senegal).
Acrylic acid, puriss, CAN.
Nitric Acid (Molar Solution).
Ethanol.

2.2 Methods

2.2.1 Grafting by (CAN)

Weight GA and added 75 mL of deionized water, stirred magnetically under nitrogen for five minutes, added 0.05 gram of (CAN) in nitric acid stirred fifteen minutes to make possible consistence of free radical on GA, followed by addition drop wise of acrylic acid. Complete the volume to100 mL using deionized water. The grafting executed at 30 °C for three hours. The solution was cooled, clean with water ethanol many times to extract homopolymer and monomer did not react. The product dried in 38°C to a constant weight.

2.2.2 Graft Copolymerization by Laser

Weight GA and added 75 mL of deionized water, stirred magnetically under nitrogen for five minutes. Irradiated with laser for 60 minutes, add acrylic acid, complete the volume to100 mL using deionized water. The grafting executed at 30 °C for three hours. The solution was cooled, clean with water ethanol many times to extract homopolymer and monomer did not react. The product dried at 38°C, and then %GE and %GY calculated from equations (Eromosele & I., 1994).

\[
% \text{GE} = 100 \left( \frac{W_2 - W_1}{W_1} \right) \quad \text{.........(1)}
\]

\[
% \text{GY} = 100 \left( \frac{W_2 - W_1}{W_3} \right) \quad \text{.........(2)}
\]

W₁, W₂ and W₃ denote weights of Gum Arabic, graft copolymer and monomer, respectively.
3. Result and Discussion

3.1 Graft Copolymerization by (C.A.N)

Grafting by (C.A.N) was achieved by at various conc. of Gum Arabic, monomer temperature and reaction time obtaining the optimal condition for grafting.

Optimum conditions:

0.05 gram CAN, 0.2 gram acrylic acid (monomer) at 30°C and time three hours, as in figure 2.

![Graph showing % GE & % GY over time (hr)](image)

**Figure 2:** Effecting Reaction Time of Grafted Copolymer, Acrylic Acid, and CAN

We study of exposure time of diode laser as in figure (3). The initial increases in curves when the time up to sixty minutes and then therefore partial hydrolysis and dissolution of GA -g- Acrylic Acid chains.

Employing laser light was an effective procedure for initiating grafting of GA compare with using C.A.N.
Figure 3: Effect Exposure Time of Laser on (%GE) and (%GY) of GA-g-Acrylic acid

3.2 FTIR of GA-G- Acrylic Acid

Proof of graft copolymerization obtained from increasing the weight of grafting polymer compared with Gum Arabic.

Figures (4) represent FTIR of Gum Arabic, acrylic acid and Gum Arabic grafted acrylic acid respectively. The spectra of Gum Arabic represent a wide beak at 3421 cm\(^{-1}\) for glucosidic ring. Also band in 2934 cm\(^{-1}\), due to C–H vibration (Sorna Prema Rajendran & Kandasamy Sengodan, 2017).

In case of acrylic acid, region between 4000-500 cm\(^{-1}\). The peak characteristic in 2949 cm\(^{-1}\) for O–H stretching, band in 2350 cm\(^{-1}\) is considered to CO\(_2\) vibration. peaks from 1699 cm\(^{-1}\)- 1630 cm\(^{-1}\) for \(\nu_{C=O}\), and peak in 1429 cm\(^{-1}\) attributed to plan bending of C-H\(_2\).

Figure (4) present bands between 1257-1065 cm\(^{-1}\) for C–O stretching vibrations, and peaks in 989 and 963cm\(^{-1}\) for bending CH\(_2\). While Acrylic Acid grafting in Gum Arabic we observed presence of an additional sharp band at 2350 cm\(^{-1}\) for CO\(_2\) vibration, show that the graft of acrylic acid had taken place.

GA spectrum in the region between 2000-1250 cm\(^{-1}\) showed peak at 1610 cm\(^{-1}\) for C-O-O asymmetric stretching. When acrylic acid graft in Gum Arabic, another additional peak is appeared at 1737 cm\(^{-1}\) and the strong peak of GA 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 presence of grafting. Acrylic Acid
appear peaks in 1699 cm\(^{-1}\), 1629 cm\(^{-1}\) for \(\nu_{C=O}\), C=C. peaks in 1737 cm\(^{-1}\) and 1645 cm\(^{-1}\) (Awwad and Albiss, 2015).

![Graph showing FTIR spectra](image)

**Figure 4a:** FTIR spectra of GA, Acrylic Acid, and GA-g-Acrylic Acid

### 3.4 XRD

Fig. (5-a, b) illustrated the powder X-ray diffractograms of GA, and GA-g-Acrylic Acid. The XRD represent the amorphous nature of GA. From figure (5a), the maximum intensity was obtained at \(\theta = 19.857^\circ\) (\(\theta\) is the angle of incidence). The peak coincide to \(\theta = 19.857^\circ\), has the length \(d\)-space = 4.4375\(\AA\).

After carrying out the grafting of GA with acrylic acid, the peak was shifted considerably to \(\theta = 20.4^\circ\) which has length \(d\)-space = 4.818\(\AA\). Figure (5b) shows that the grafting decreases the intensity of the corresponding peak. The grafting sample turns into amorphous. The grafting of acrylic acid occurs over the GA chain.
3.5 SEM

The surface of the GA-g- acrylic acid was studied by SEM. The exterior surface of the GA-g- 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 graft of acrylic acid on the GA as shown in Fig (6-a,b).

Figure 6-a, b: Typical SEM Images of (a) Gum Arabic Before Grafting and (b) GA-g- Acrylic Acid
3.6 Thermogravimetric Analysis (TGA)

Figure (7-a, b) and table (1) illustrate thermal behavior of Gum Arabic, and grafted copolymer. The small weight loss (16%) up to 255°C and (9%) up to 245°C for Gum Arabic and grafted copolymer.

Gum Arabic present 3 stages, first stage is for desorption of dampness in water to the GA structure, however the 2 and 3 stages due to molecular degradation and decomposition reactions of GA. Weight loss was slower in GA-g-acrylic acid, so that it is thermally stable than the GA.

**Table 1**: Thermogravimetric Information with Heat at 10 °C/min under Nitrogen for Gum Arabic and GA-G-Acrylic Acid

| Sample                  | Stages number | Temperature (°C) | % loss of Weight |
|-------------------------|---------------|-----------------|------------------|
| GA                      | 1             | 55-255          | 16               |
|                         | 2             | 255-410         | 66               |
|                         | 3             | 410-720         | 20               |
| GA-g-acrylic acid       | 1             | 55-245          | 9                |
|                         | 2             | 300-720         | 82               |

**Figure 7-a, b**: TGA Curves of (a) Gum Arabic and (b) GA-g-Acrylic Acid
4. Conclusions

The optimum conditions for grafting GA-g-acrylic Acid when used laser as initiator, were 0.5 gram of gum, 0.2 gram acrylic acid, 0.05 gram of (CAN), reaction temperature 30° C, and reaction time 180 min. Optimum percentages of graft yield and graft efficiency was 97%, 28% for GA-g-acrylic acid.

In the future more studies will be conducted for graft copolymer such as study application of grafted copolymer in drug delivery system, using the synthetic graft copolymer as carriers for microencapsulation of oils and other bioactive molecules, and in the nanotechnology and nanomedicine fields, therefore its biocompatibility in vivo applications, and its stabilization of nanostructures.

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