



RESEARCH ARTICLE

COMPARISON ON THE REACTIVITY OF CERIUM(IV) AMMONIUM NITRATE AND GREEN LASER INDUCED GRAFT COPOLYMERIZATION OF 3,3-DIMETHYL ACRYLIC ACID ONTO KARAYA GUM

Mohamed Gusm Alla M. Sulamain*^{1,2}, Mohamed Shaker S. Adam*³, Essam Elgeily A. Ali^{1,4} and Hayat Z. E. Elbasheer¹

¹Chemistry Department, Faculty of Applied & Medical Sciences and Scientific Departments, Taif University

²Faculty of Education - Alzaiem Alazhari University, Khartoum / Republic of Sudan

³Department of Chemistry, Faculty of Science, Sohag University, Sohag Egypt

⁴Physics Department, College of Science and Technology, Shendi University, Shendi, Republic of Sudan

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ABSTRACT

Karaya Gum (KG) has been modified by graft copolymerization with 3,3-dimethyl acrylic acid in aqueous media initiating by diode laser (532 nm) or by cerium(IV) ammonium nitrate. The optimum reaction conditions to afford maximum and efficient graft copolymerization initiated by laser were 60 minutes laser irradiation time, 0.5 g of KG and 0.20 g of 3,3-dimethyl acrylic acid, whereas, those initiated by cerium(IV) ammonium nitrate (CAN) where 3 h of the reaction, 0.5 g of KG, 0.20 g of 3,3-dimethyl acrylic acid at 30 °C. The grafting ratio and homopolymer have been determined for both. The percentages of graft efficiency and of graft yield were 36% and 90%, respectively, using laser beam and were 26% and 76%, respectively, using CAN. 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 KG-g-3,3-dimethyl acrylic acid. The laser irradiation was found to be effective and green tool for producing KG-g-3,3-dimethyl acrylic acid (graft polymer).

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INTRODUCTION

Karaya Gum (KG) is a naturally occurring gum obtained from *Sterculia urens*, or by one of its common names, Indian tragacanth, mucara, sterculia, or Bassora tragacanth [1]. In Sudan and elsewhere in Africa, KG can be obtained from *Sterculia setigera*. *Sterculia setigera* is a multi-purpose savanna tree which spreads naturally in central and southern Sudan [1-3].

KG is a partially acetylated complex having around 8% acetyl group and about 37% uronic acid residues [4]. The polysaccharide component of KG has a high molecular weight and is composed of galacturonic acid, -D-galactose, glucuronic acid, L-rhamnose, and other residues [5]. The natural polysaccharide polymers, *i.e.* KG, are been reported for their application in pharmaceutical and biomedical fields for the controlled release of drugs [6]. They do gain certain properties over synthetic polymers, *e.g.* nontoxic, biodegradable, less expensive, and without stinting available compare to the synthetic polymer [7]. Modification of polymer by either 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 [8,9].

Grafting provides convenient method for tailoring material properties to specific end uses [10,11]. Grafting of Poly methacrylic acid onto KG has been studied with the objective of improving and modifying the properties of KG. A new material is made by combining the properties of both natural and synthetic polymer. It swells in water and thus used as release rate controlling polymer in different drug delivery system [12]. 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 [13]. Crosslinked chitosan/poly methacrylic acid graft copolymer was used as adsorbent for both Cu²⁺ ions and hepatitis A virus [14] and water solubility [15]. Recent study reveals that the grafting of methacrylic acid onto gelatin [16], starch, carboxymethyl starch demonstrate pH-responsiveness character, swelling behaviour that has create application in drug delivery and for amine activator [17]. For the last few decades, chemical modification of Arabic Gum (AG) by graft copolymerization of vinyl monomers onto it has been a subject of academic as well as industrial interest. Various initiating systems are employed through graft copolymerization of different monomers onto AG, *e.g.*, cerium(IV) ammonium nitrate (CAN), persulfate, microwave and radiation, etc. Less attention has been paid to the grafting

*Corresponding author: Mohamed Gusm Alla M. Sulamain

Chemistry Department, Faculty of Applied & Medical Sciences and Scientific Departments, Taif University

of AG by laser. AG used in graft copolymerization usually need to be heated in all cases [18].

In the present work, diode laser with wavelength of 532 nm and output power of 200 mW was used to initiate graft copolymerization of 3,3-dimethyl acrylic acid onto KG. On the other that graft copolymerization is compared that using CAN. Various investigation tools were applied to ensure the success of the process.

Experimental

Materials

Karaya Gum (KG) was collected from South Kordfan region, Sudan during season 2013 and used after cleaning from park, leaves and extraneous materials without further purification. Also other chemical compounds were supplied from Fluka Company, 3,3-dimethyl acrylic acid, puriss, cerium(IV) ammonium nitrate (CAN), nitric acid (1.0 mol dm⁻³ solution) and ethanol, which used as received.

Equipments

The equipments used in this study were a diode laser with wavelength of 532 nm and Power of 200 mW, supplied from USA. 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 D8 Advance, Germany, equipped with a θ -goniometer under the following operation conditions: 40 KV and 40 mA with CuK α -radiation at 1.54056 Å. The relative intensity was recorded in the scattering range (2 θ) of 4–60°. Scanning Electron Microscope (SEM), supplied from JEOL, Japan, model 840 Å. Thermogravimetric analysis system (TGA) supplied from Shimadzu (Japan) at a heating rate of 10 °C/min.

METHODS

Graft Copolymerization by CAN

The graft copolymerization of 3,3-dimethyl acrylic acid onto KG was carried out under different reaction conditions with 1.0 x 10⁻³ mol dm⁻³ of the monomer (CAN) to obtain the optimum condition of graft copolymerization, as reported previously [18,19]. In this study the graft copolymerization method follows, 0.5 g of KG was dissolved in 75 mL of distilled water under stirring in dried conditions (under passing nitrogen gas through the solution) for 5 minutes. The required amount of (1.0 x 10⁻³ mol dm⁻³) CAN in 1.0 mol dm⁻³ of nitric acid was added dropwise to the KG solution with continuous stirring for 15 minutes to facilitate the formation of free radical sites on the KG chain. Finally, a definite amount of 3,3-dimethyl acrylic acid was added dropwise to the reaction mixture under continuous stirring in dried conditions. The total volume of the final reaction mixture was completed to 100 mL by distilled water. Then the polymerization process was preceded at 30 °C for 3 hours. The reaction mixture was allowed to cool down and the graft copolymer which precipitated was filtered off. The precipitate washed many times with distilled water: ethanol (20: 80) to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The grafted copolymer was dried under

vacuum oven at 40 °C and then weighed, as reported similarly elsewhere [18].

Laser Induced Graft Copolymerization

Similar to the above procedure, 0.5 gram of KG was dissolved in 75 mL of distilled water, and then it was magnetically stirred under nitrogen for 5 minutes. The resulting solution was initiated and irradiated by a monochromatic diode laser beam (532 nm) for 60 minutes. After that, 0.02 mol dm⁻³ of 3,3-dimethyl acrylic acid was added dropwise. The total volume of the reaction mixture was completed to 100 mL by distilled water. Then, the polymerization process was preceded at 30 °C for 3 hours. The reaction mixture was allowed to cool down and the graft copolymer was filtered off, washed many times with distilled water : ethanol (20 : 80), dried under vacuum oven at 40 °C and then weighed, as repeated above.

Graft efficiency, Graft yield, Graft ratio and Homopolymer

The percentage of graft efficiency (% GE) and percentage of graft yield (% GY) of the final dried product were deduced according to Fanta s definition [20] and to the following equations [21] and collected in Table 1:

$$\begin{aligned} \% \text{Graft efficiency (\% GE)} &= 100 [(W_2 - W_1) / W_1] & (1) \\ \% \text{Graft yield (\% GY)} &= 100 [(W_2 - W_1) / W_3] & (2) \\ \% \text{Graft ratio (\% GR)} &= 100 [W_2 / W_1] & (3) \\ \% \text{Homopolymer (\% H)} &= [100 - \% \text{GE}] & (4) \end{aligned}$$

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

RESULTS AND DISCUSSION

Graft copolymerization of 3,3-dimethyl acrylic acid (monomer) onto KG initiated with CAN was carried out depending upon different concentrations of CAN at different temperatures and various times to optimize the reaction conditions. The optimum conditions were 0.5 g of KG, 0.20 gram of 3,3-dimethyl acrylic acid at 30 °C in 3 h. The percentage of graft efficiency and graft yield at the optimum conditions were 26% and 76%, respectively (Table 1 and Fig. 1). While the optimum conditions using laser irritation (532 nm) were 0.5 g of KG and 0.20 g of 3,3-dimethyl acrylic acid at 30 °C in 60 min. The percentage of graft efficiency and percentage of graft yield at the optimum conditions were 36% and 90%, respectively (Table 1 and Fig. 2).

Table 1 Effect of CAN and laser on the graft copolymerization of 3,3-dimethyl acrylic acid on KG.

	Graft efficiency (% GE)	Graft yield (% GY)	Graft ratio (% GR)	Homopolymer (% H)
CAN	26	76	340	74
Diode laser (532 nm)	36	90	315	64

The apparent acceleration in the percentage of graft efficiency and graft yield may be attributed to the gel effect [22], resulting from an enhanced solubility of poly 3,3-dimethyl acrylic acid in the monomer.

The effect of exposure time of diode laser in the percentage of graft efficiency and graft yield of KG-g-3,3-dimethyl acrylic acid was illustrated in Table 1 and Fig. 2. The graph is characterized by initial increases in percentage of graft efficiency and graft yield with exposure time of the laser up to 60 min. With increasing the irradiation time the percentage of

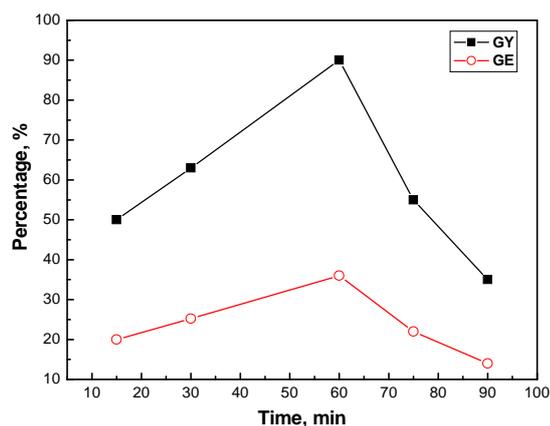


Fig. 1 Effect of reaction time on percentages of graft efficiency () and of graft yield () of KG-g-3,3-dimethylacrylic acid (3,3-dimethyl acrylic acid = 0.02 mole dm⁻³, CAN = 0.91 x 10⁻³ in 100 mL aqueous solution for 3 h at 30 °C).

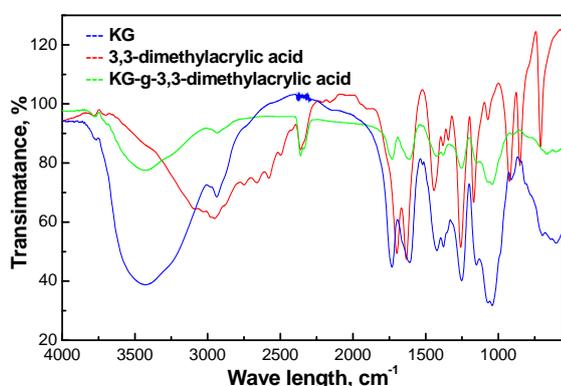


Fig. 2 Effect of reaction time on percentages of graft efficiency () and of graft yield () of KG-g-3,3-dimethylacrylic acid (3,3-dimethyl acrylic acid = 0.020 mole dm⁻³, in 100 ml aqueous solution for 60 min at 30 °C).

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, as observed elsewhere for the diode laser induced grafting of 3,3-dimethyl acrylic acid onto karaya gum [18]. It is of interest to illustrate that the percentage of graft efficiency and graft yield in case of diode laser induced graft copolymerization were 36% and 90%, respectively.

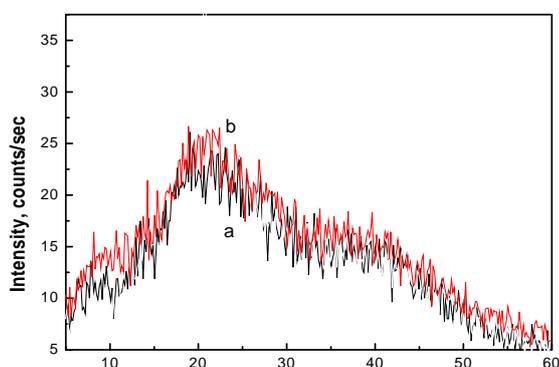


Fig. 3 FTIR spectra of KG (), 3,3-dimethyl acrylic acid () and KG-g-3,3-dimethyl acrylic acid () in the range from 4000 to 500 cm⁻¹.

Employing laser was an efficient and more friendly environmentally (green) method for initiating graft copolymerization of 3,3-dimethyl acrylic acid on KG.

According to the graft copolymerization of 3,3-dimethyl acrylic acid onto KG using CAN and laser irradiation results which present that the graft copolymerization with laser irradiation is more effective than that with CAN, we highlight here on the characterization of the more effective graft copolymerization of 3,3-dimethyl acrylic acid onto KG using laser irradiation (532 nm). The graft copolymerization of 3,3-dimethyl acrylic acid onto KG using CAN is standard and representative process which applied only for comparison with the new graft copolymerization by laser irradiation [18,19].

FTIR spectra

As maintained above the evidence of grafting has been obtained during the graft copolymerization of different ratios of 3,3-dimethyl acrylic acid onto KG, 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 KG, 3,3-dimethyl acrylic acid and KG grafted 3,3-dimethyl acrylic acid. The reported similar work which has been achieved by us, shows the main vibration bands of unmodified KG, acrylamide and KG-g-AAm, respectively [18,19]. KG 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 2812 cm⁻¹ were attributed to the symmetric stretching of C-H₂ and vibration of stretching C-H [22,23].

Comparing to the recent results, the FTIR spectrum of 3,3-dimethyl acrylic acid, was recorded between 4000-500 cm⁻¹ shows that the broad absorption band of 3,3-dimethyl acrylic acid has maximum absorption band located at 2949 cm⁻¹ for O-H stretching band, as reported before of the KG grating with acrylamide [18]. The weak peak observed at 2350 cm⁻¹ is due to the CO₂ vibration. The band between 1698 cm⁻¹-1629 cm⁻¹ are due to the 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. The analysis of the spectra shows that the bands between 1257 and 1064 cm⁻¹ are assigned to C-O stretching vibrations, while the bands at 988, 961cm⁻¹ are assigned to plan bending CH₂. When KG was grafted by 3,3-dimethyl acrylic acid, there is an additional sharp peak at 2361 cm⁻¹, in comparison to the spectrum of the substrate and KG, indicated that grafting had taken place. This peak might be assigned to the CO₂ vibration. FTIR spectrum of KG shows two peaks at 1731 cm⁻¹ and 1610 cm⁻¹ which are attributed to the C=O stretching and C=C stretching, respectively. When KG was grafted by 3,3-dimethyl acrylic acid, the absorption band of grafted KG at 1610 cm⁻¹ 1731 cm⁻¹ has the same position as in case of KG before grafting with less optical density for the grafted gum. The 3,3-dimethyl acrylic acid has two peaks in the same region at 1698 cm⁻¹, 1633 cm⁻¹, these two peaks are due to the C=O, C=C stretching and in plan bending of C-H₂. The shift of these two peaks to 1731 and 1610 cm⁻¹ in grafted

KG are elucidated the grafting. Within the range of 1500-500 cm^{-1} the vibrational bands of 3,3-dimethyl acrylic acid are appeared in the case of grafted copolymer.

It can be observed that the variations between untreated KG and grafted KG are similar with less optical density of the bands of grafted KG. It is also observed that there is a decreasing in the optical density for all other shoulders in the range from 880-500 cm^{-1} . This indicated that the KG was grafted with 3,3-dimethyl acrylic acid.

X-ray Diffraction (XRD)

Figure 4 illustrates the powder X-ray diffractograms obtained for the natural KG, before and after graft with 3,3-dimethyl acrylic acid irradiated by laser beam (532 nm) respectively. The XRD pattern shows the amorphous nature of KG. The maximum intensity is at $2\theta = 20^\circ$ which well agreed with values reported in literatures [18,19], as shown in Fig. 4.

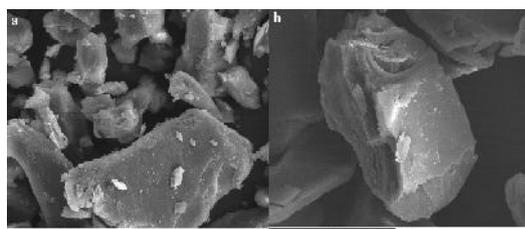


Fig. 4 XRD of KG (a) before grafting () and (b) after grafting with KG-g-3,3-dimethyl acrylic acid ().

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 grafting copolymerization of KG by 3,3-dimethyl acrylic acid, 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 KG. Particularly, Figure 4 shows that the graft decreases the intensity of the corresponding peak because the graft copolymer becomes almost amorphous. Consequently, The graft of 3,3-dimethyl acrylic acid is taken place randomly along the KG chain, giving rise to a random copolymer. This will efficiently destroyed the regularity of the packing of the original KG chains, which results in the formation of amorphous copolymer.

Electron Microscope Scan (SEM)

Morphological examination of the fine powder of KG and grafted co-polymerized KG-g-3,3-dimethyl acrylic acid was carried out using SEM by making a thin film of desirable size on copper grids and coated with gold. The surface topography of the KG-g-3,3-dimethyl acrylic acid studied by SEM and compared that with the GK surface. The exterior surface of the KG-g-3,3-dimethyl acrylic acid appears as heterogeneous irregular rocky surface and clearly different from that of the parent KG, which has big rocky shape of smooth surface with different sizes. Hence, the surface change morphology of the modified KG is clear in the in the SEM and some crosslinked networks have been observed.

This observation supports the grafting of 3,3-dimethyl acrylic acid onto the KG surface, as shown in Fig. 5. Similar porous structure and shape has been reported for the grafting of polyacrylamide onto gum arabic initiated by laser beam [18]. Finally, Fig. 5b showed that there is no any crystals of the

unreacted 3,3-dimethyl acrylic acid on the surface of the graft copolymer.

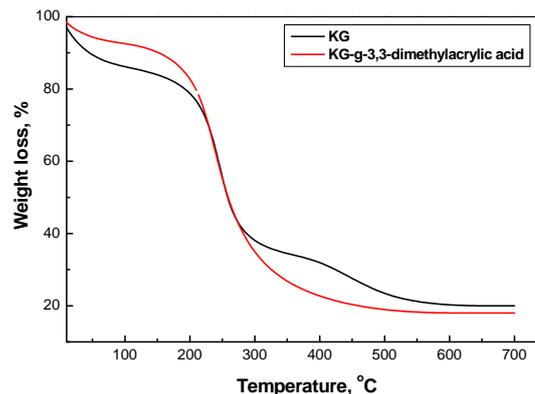


Fig. 5 Typical SEM images of KG before grafting (a) and after grafting with 3,3-dimethyl acrylic acid (KG-g-3,3-dimethyl acrylic acid) (b).

Thermo gravimetric Analysis (TGA)

In this study TGA was applied on the dried samples in air with a heating rate of 10 $^\circ\text{C}/\text{min}$. Figure 6 and Table 2 illustrate the details of thermal behavior according to the primary thermo grams and derivative thermo grams for KG and KG-g-3,3-dimethyl acrylic acid. The samples showed first a small weight loss (15%) up to 250 $^\circ\text{C}$ and (8%) up to 240 $^\circ\text{C}$ for KG and KG-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, as observed elsewhere [4, 19].

Table 2 Thermogravimetric data of KG and KG-g-3,3-dimethyl acrylic acid during heating rate at 10 $^\circ\text{C}/\text{min}$ under nitrogen atmosphere

Sample	Number of stage	Temperature range ($^\circ\text{C}$)	Weight loss (%)
KG	1	50-250	15
	2	250-400	65
	3	400-700	80
KG-g-3,3-dimethyl acrylic acid	1	50-240	8
	2	300-700	82

This is not unexpected taking into account the hydrophilic nature of the composite constituents. It should be noted that the thermogram of the KG 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 KG [13,18]. It was observed that the weight loss was slower in the case of the graft copolymer, in between 30 to 700 $^\circ\text{C}$, indicating that the graft copolymer is more thermally stable than KG, as shown in Fig. 6.

CONCLUSIONS

Modification of Karaya Gum (KG) by graft copolymerization with 3,3-dimethyl acrylic acid initiating by diode laser (532 nm) or by cerium(IV) ammonium nitrate (CAN) has been studied. The copolymerization by diode laser irradiation is more effective than by an aqueous solution of CAN. The percentages of graft efficiency and of graft yield were 36% and 90%, respectively, using laser beam and were 26% and 76%, respectively, using CAN. 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 successful co-polymerization processes.

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