

Research Article

Carboxymethylation of *Anacardium Occidentale* L. Exudate Gum: Synthesis and Characterization

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Abstract: The use of natural gums taken from the exudates and extracts of plants has been given a strong impulse due to the lucrative possibilities for industrialization and excellent international market. *Anacardium occidentale* L gum consists of highly branched galactan framework comprising of chains of (1-3) – linked with β -D-galacto pyranosyl units interspersed with β -(1-6)-linkages, possessing hydroxyl groups available for the attachment of biologically active compounds. The modification discussed includes the introduction of carboxymethyl groups into the molecules for extending the applications of partially carboxymethylated *A. occidentale* gum. The carboxymethylation conditions with respect to the volume and concentration of sodium hydroxide, weight of chloro-acetic acid in a reaction temperature were optimized. The solubility of modified gum was higher than the unmodified gum. The resulting product was characterized by FTIR spectroscopy. The carboxymethylated gum may provide an efficient alternative approach for the oral delivery of hydrophilic macromolecules.

Keywords: *Anacardium occidentale*, gum, modification, carboxylmethyl group

INTRODUCTION

Exudate gums are heteropolysaccharide complex carbohydrate with high molecular weight. They are sticky substances which exude from certain plants either as a result of mechanical injury or a microbial infection [1]. Due to excellent properties of gum such as solubility, viscosity, thickening, stabilizing and emulsifying, they are utilized in an overwhelming number of applications, ranging from adhesive, beverages, confectionaries, cosmetic, paint, paper, food and most importantly pharmaceuticals [2-4].

Cashew gum is chemically composed of 61% galactose, 14% arabinose, 7% Rhamnose, 8% glucose, 5% glucuronic acid and less than 2% other sugar residue [5, 6]. Hydrolysis of cashew gum yields L-arabinose, L-Rhanose D-galactose and glucuronic acid. The gum has a highly branched galactan frame work comprising of chains of (1-3)-linked with β -D-galactopyranosyl units interspersed with β -(1-6)-linkages [2].

Even though with all these properties and wide range of applications earlier mentioned, there are still evidence of some drawbacks such as uncontrolled rate of hydration, pH dependency, thermal decomposition, low shear stress resistance, syneresis, just to mention

but a few which limit the usage of the gum and other natural polysaccharides [7].

Chemical modifications such as oxidation, acetylation, hydroxyl-propylation, carboxymethylation and cross-linking provide efficient route not only to reduce the drawbacks but also to improve on the physicochemical properties and to introduce new properties for different applications.

Possible processing methods for *Anacardium occidentale* gum depend on chemical modifications aimed at developing functional characteristics that make this material versatile and useful in a variety of applications. Native cashew gum can be modified into water - soluble derivatives by using reactive groups to substitute the free hydroxyl groups along the macromolecule backbone [8].

Upon dissolution in water, gum may give rise to as much as 10-14% insoluble residue as depending on gum purity [9].

Some investigation have been undertaken to deal with the solubility properties of gum as faster and better solubility in water, as well as multifunctional characteristics can be obtained by the introduction of

different compounds [10]. The simplest change is achieved by a purification method for removing the insoluble fractions, as well as by the synthesis of cashew gum derivatives, such as hydroxypropyl cashew gum, acetylated cashew gum and carboxymethyl cashew gum, which may obviate the above – mentioned problems [7].

Carboxymethylation of polyisaccharides is a widely studied conversion since it is simple and leads to products with a variety of promoting properties. Carboxymethyl polysaccharides exhibits improved solubility and has been used in the food, cosmetic, detergent, paper, pharmaceutical and textile industry [11].

Carboxymethylation generally increases the hydrophilicity and solution clarity of the polysaccharides [12]. This high soluble polymer is a good candidate for preparation of different novel drug delivery like beads, microparticules or nanoparticles. The aim of this work is to prepare and characterize carboxymethyl *Anacardium occidentale* gum in order to improve its physicochemical characteristics (solubility). The result of this research is likely to highlight the effect of carboxymethylation on the solubility of *Anacardium occidentale* gum in order to amplify the possibilities of the gum in oral delivery of hydrophilic macromolecules.

MATERIALS AND METHOD

Anacardium occidentale gum was collected by tapping in March, 2010 from Owena Forestry, Ondo State, Nigeria. Superficial incision was made at the bark of the tree and the bark was later stripped off. After five weeks, gum was manually collected. The gum sample were dried at room temperature, cleaned, milled with Kenwood blender and sieved through a mesh-size 250 microns obtain fine – size particles, kept in labeled plastic container and stored in the refrigerator for subsequent analysis.

Purification of Gum Sample

Dried crude gum (10g) was stirred in cold distilled water 250 ml for 2 – 3 hours at room temperature. The

supernatant was obtained by centrifugation. The supernatant was made up to 500ml and treated with ethanol 1.4v/v in order to precipitate the carbohydrate. The material was washed again with ethanol followed by distilled water and freeze-dried.

Preparation of Carboxymethylation

Gum was derivatized to sodium carboxymethyl gum by mixing it with 4 ml distilled water heated to 80°C for 15 minutes and cooled. Then 56% w/v of ice-cold sodium hydroxide solution was added drop wise over a period of 45 minutes. Monochloro-acetic acid solution was added slowly for a period of 1 hour to the above mixture and maintained at 15°C. The temperature of the mixture was raised slowly to 65°C and stirred for another 1 hour. The wetted mass was washed with methanol for 15 minutes. The pH of the suspension was adjusted to neutrality with glacial acetic acid. Then it was dried at 50-60°C.

Solubility

The solubility of gums was determined. Gum sample, 10g was suspended in 40 ml of distilled water. It was heated to the desired temperature (60°C, 70°C or 80°C) for 30 minutes with continuous shaking. The mixtures were centrifuged at 1000rpm for 15 minutes. An aliquot of supernatants (5ml) were evaporated at 130°C and weighed. The solubility's of the gums were the percentage ratio in mass (g) of the dried supernatant to the initial mass (g) of the dry gums.

Fourier Transform Infra Red (FTIR) Spectroscopy

FTIR spectra were obtained on a FTIR spectrometer (Shimadzu 8400s) using a KBr disc. The equipment was operated with a resolution of 4 cm⁻¹ and the scanning range from 4000 to 370 cm⁻¹.

Statistical Analysis

The data obtained from the study were analyzed using the Statistical Analysis System (SAS) software and the means were separated by T-Test.

RESULTS AND DISCUSSION

Table 1: Physicochemical characteristics of carboxymethyl and native *Anacardium occidentale* gum

Type	Temperature	Solubility (%)
Native gum	60°C	3.40 ± 0.04
	70°C	23.21 ± 0.06
	80°C	40.10 ± 0.03
Carboxymethyl gum	60°C	56.70 ± 2.05
	70°C	102.42 ± 6.26
	80°C	124.32 ± 4.80

Mean ± S.D, n = 3

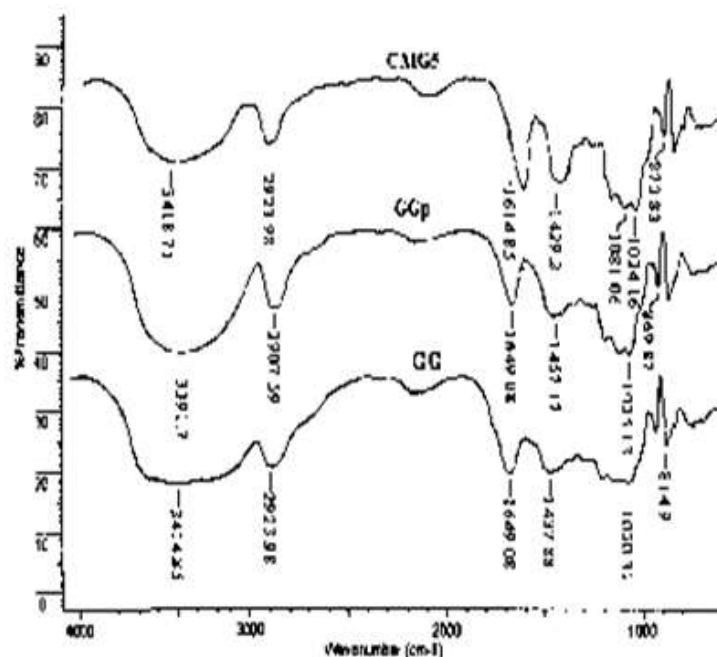


Fig. 1: FTIR Spectra of native gum (GG), Purified gum (GG_p) and carboxymethyl gum (CMCG)

The solubility of modified and unmodified gum profoundly increased with increase temperature. From Table 1, the solubility of the carboxymethylated gum was higher than native gum and at temperature above 80^oc more than 100% modified gum were dissolved. This is due to introduction of carboxymethyl groups which is bulkier than hydroxyl groups and capable of obstructing chain association.

The superior solubility of carboxymethyl gum compared with the native gum may be due to the presence of hydrophilic substituting groups (-CH₃CO-) which allow the retention of water molecules because of their ability to form hydrogen bonds [13]. The IR spectra of raw guar gum (GG), purified guar gum (GG_p) and carboxymethyl gum (CMCG) are show in Fig. 1 above.

The presence of a very strong and broad absorption band at 3391cm⁻¹ is assigned to OH bond stretching while the sharp absorption band located at 2907 cm⁻¹ may be attributed to CH group stretching. The absorption band appearing at 1649 cm⁻¹ is due the OH bond belonging to water molecules. CH₂ group bending is assigned to an absorption band located at 1457 cm⁻¹, and the bending of CH₂-O-CH₂ appears in the 1025 cm⁻¹ frequency region. A slight modification can be observed in the well-defined spectrum of purified gum. The IR spectrum of carboxymethyl gum (CMCG) shows a reduced intensity of the absorption band located at 3418 cm⁻¹, due to OH stretching, indicating that some OH groups were carboxymethylated. The band due to water (bending of water), which appear at approximately 1650 cm⁻¹ in the GG_p sample was absent in the CMCG sample. The

asymmetrical and symmetrical vibrations due to moiety were assigned to 1615 and 1429 cm⁻¹, respectively, which may be attributed to the incorporation of carboxymethyl groups into the gum molecule.

CONCLUSION

The study confirms that purification by extraction and carboxymethylation may improve the physicochemical properties (solubility) of *Crude Anacardium occidentale* gum. The feasibility of the procedure was demonstrated by FTIR spectroscopy. Furthermore, the obtained product can have wider biological application as drug delivery carriers by grafting or cross-linking compounds of interest.

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