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Preparation and characterization of carboxymethyl *Sweitenia mycrophylla* gum. A potential exicipient

[1]O. Adeyanju*, [2]A.O Edah, [3]Y. Hussaini, [4]A.I. Adejoh and [5]U.C Nwanta

[1,2,4,5]Department of Chemistry, University of Jos, Nigeria
[3]Department of Science Laboratory Technology, Federal College of Forestry, Jos, Nigeria
*Corresponding Author: adeyanju.olusola@yahoo.com

Abstract

Sweitenia mycrophylla gum was chemically modified via carboxymethylation. The product was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Energy Dispersive X-ray (EDX) and Nuclear Magnetic Resonance (NMR). Physicochemical characterization of the native and carboxymethyl gum such as viscosity, solubility and swelling power were also determined. The modified gum with the degree of substitution 0.24 had higher physicochemical properties than the native gum. The result showed that chemical modification via carboxymethylation may improve the viscosity, solubility and swelling power of gum which may result in higher efficacy for effective utilization in gum-based industries.

Keywords: Carboxymethyl groups, *Sweitenia mycrophylla,* gum, excipient.

1. Introduction

Modified polysaccharides such as gums and starches have played a major role in the food and pharmaceutical industries over the past few decades. They possess unique properties not found in natural polysaccharides, which are suitable for the development of new improved products [1]. Carboxymethylation of polysaccharides is a widely studied conversion since it is simple and leads to products with variety of promising properties [2].

In general, the polysaccharide is activated with aqueous alkali hydroxide mostly sodium hydroxide and converted with monochloroacetic acid or its sodium salt according to the polysaccharide derivatives. Not only cellulose and starches have been applied as starting materials [3,4].

The polysaccharide gums represent one of the most abundant industrial raw materials and have been the subject of intensive research due to their sustainability, biodegradability and biosafety[5]. *Swetenia mycrophylla* gum is non-starch polysaccharides obtained from the bark of *Sweitenia mycrophylla* tree, a large tree reaching a height of 30-40m and a girth of 3-4m, in favourable condition, it can reach 60m high and 9m girth [6,7].

The physicochemical, toxicological, structural characterization and application of purified S. *mycrophylla* gum had been carried out in our previous studies [8-11]. Hence, this research aims at investigating the carboxymethylation of the gum in order to improve its physicochemical characteristics for better efficacy in industrial application. The results of this research is likely to highlight the effect of chemical modification by carboxymethylation on the physicochemical properties of the gum from *Sweitenia mycrophylla*.

2. Materials and Methods

2.1 Purification of Gum Sample

Dried crude gum (10g) was stirred in cold distilled water (250ml) for 2 hours at room temperature. The supernatant was obtained by centrifugation and made up

to 500ml and ethanol solution was added (1:4 v/v) to precipitate all the carbohydrate. The precipitated material was washed again with ethanol, followed by distilled water and dried at room temperature milled with Kenwood blender (UK) and later sieved using a bin (Mesh size-250microns) kept in labeled plastic container for subsequent analysis.

2.2 Preparation of Carboxymethyl Gum

Gum was derivatized to sodium carboxymethyl gum by mixing it with 4ml distilled water heated to 80^0C for 15 minutes and cooled. Then 56% w/v of ice-cold sodium hydroxide solution was added drop wise over a period of 45minutes. Monochloro-acetic acid solution was added slowly for a period of 1 hour to the above mixture was raised slowly to 65^0C 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 50-60^0C.

2.3 Physicochemical Analysis of native and Carboxymethyl *S. mycrophylla gum*

2.3.1 Solubility

The solubility of the gum was determined. Gum sample, 10g was suspended in 40ml of distilled water. It was heated to the desired temperature (60^0C, 70^0C or 80^0C) for 30 minutes with continous shaking. The mixtures were centrifuged at 1000 rpm for 15 minutes. An aliquout of supernatants (5ml) was evaporated at 130^0C and weighed. The solubility's of the gums was the percentage ratio in mass (g) of the dried supernatant to the initial mass (g) of the dry gums.

2.3.2 Swelling Capacity

The swelling capacity was determined using the modified method of [24]. Tapped volume (V_t) occupied by 5g (125μm powder) sample placed in 100ml graduated cylinder was determined by mechanical (500 taps) tapping the bottom of the cylinder and 50ml distilled water was added after. The contents was allowed to stand for 24h, the new volume occupied by the sediment sample (V_s) was then measured. The percentage swelling was computed.

$$S = \frac{V_s - V_t}{V_t} \times 100 ------(1)$$

Where;
S is the % swelling capacity
V_s is the volume of swollen material
V_t is the tapped volume of the material.

2.3.3 Viscosity

The viscosity of 2% w/v gum suspension was determined using a viscometer (Brookfiled, RVDV-II$^+$PRO, USA) with a spindle No. RV-02 and a speed of 200rpm of 200 at 25^0C. the readings of viscosity were taken after 30s of rotation. All measurements were performed in triplicate.

2.4 Microstructure Studies by SEM

Morphological features of the gum was studied with a JSM-5600LV scanning electron microscope of JOEL (Tokyo, Japan). The dried sample was mounted on a metal stub and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 10kv and at 500x magnification.

2.5 X-Ray Powder Diffraction (XRD)

X-ray diffraction patterns of the gum was analysed using a Siemens D5000 X-ray diffractometer (Siemens, Munish, Germany). Powder sample, packed in rectangular aluminum cells, was illuminated using Cuk & radiation (A=1.54056 Ao) at 45KV and 40mA. Samples were scanned between diffraction angles of 5^0C to 40^0C, scan steps of 0.1 were used and the dwell time was 15.0sec. A nickel filter was used to reduce the Kp contribution to the X-ray signal. Triplicate measurements were made at ambient temperature.

2.6 Fourier Transform Infrared (FT-IR) and NMR Spectroscopy

The FT-IR spectrum of the sample was recorded in an FTIR spectrometer (Nicolet Magna-4R 560. MN USA), using potassium bromide (KBr) discs prepared from powdered samples mixed with dry KBr. C-NMR, C-DEPT and Solid State NMR of Sweitenia mycrophylla gum were recorded in an NMR (600 MHz) spectrometer (Agilent technologies, America). The sample (10mg) was dissolved in 700μL at 70^0C with continous stirring for 6hours followed by sonication for 10minutes. The sample was centrifuged and transferred to a 5mm NMR tube. Chemical shifts were reported in ppm relative to an internal standard TMSP (Tetramethylsilanepropoinic acid). Peak integra were performed using Agilent software, America.

2.7 Degree of Substitution (DS)

The degree of substitution (DS) of the carboxymethyl (CMS) sample was determined by the standard method [24]. 4 g of sample and 75ml. 95% ethyl alcohol was agitated in 250ml. beaker for 5 min to obtain good slurry. The CMS was converted to insoluble acid form by adding 5ml of concentrated nitric acid and boiled on a hotplate for 5min. The solution was then removed from hotplate and further stirred for 10min. By using vacuum pump, liquid solution was decanted and sample washed with ethanol (80%) that has been heated to 60°C for 5 times. Then the precipitate was washed with anhydrous methanol to remove acid and salts (until filtrate had no effect on blue litmus and test negative to silver nitrate solution) and apply vacuum to remove the alcohol.

Lastly, the sample was dried at 105°C for 3h and cool in desiccators. 1.5g of dry acid insoluble form carboxymethyl gum was added to 100ml of distilled deionized water and 25ml of hydroxide 0.5M with agitation. The solution was heated to boil for 15min. The excess sodium hydroxide was titrated while solution was still hot with 0.5M HCL. Phenolphthalein indicator was added to observe the color change from Mexican pink (dark pink) to colorless.

To calculate the degree of substitution, the equation below was used;

$$\text{Degree of substitution} = \frac{0.162 \times A}{1-(0.058 \times A)} \quad --(2)$$

$$A = \frac{BC - DE}{F}$$

Where;
A = milli-equivalents of consumed acid per gram of specimen
B = volume of sodium hydroxide added
C = concentration in molarity of sodium hydroxide added
D = volume of consumed hydrochloric acid
E = concentration in molarity of hydrochloric acid used
F = weight of sample used (g)

3. Results and Discussion

3.1 Results

Table 1: Physicochemical properties of the purified and carboxymethyl *S. mycrophylla* gum

	Solubility (%)		Viscosity (MPa.S)	Swelling capacity (%)
Native Gum	60^0C	10.40±0.2	22.50±0.10	7.94±0.13
	70^0C	34.10±4.4		
	80^0C	39.50±1.5		
Carboxymethyl gum	60^0C	47.80±2.6	58.70±0.30	17.64±0.34
	70^0C	80.54±5.0		
	80^0C	97.94±1.6		

Table 2: ^1H and ^{13}C NMR assignments of *S. mycrophylla* gum (10mg in 700µL, D_2O, 60^0C) Referenced to TMSP in PPM

Sugar Residue A ($\alpha - D - Galactose$)			Sugar Residue B ($\beta - D - Mannose$)		
	^1H	^{13}C		^1H	^{13}C
A1	5.40	98.87	B1	4.70	102.1
A2	3.58	71.90	B2	4.11	77.2
A3	3.75	73.00	B3	3.63	73.5
A4	4.00	74.80	B4	3.85	77.1
A5	3.95	76.00	B5	3.90	75.2
A6	3.25	63.50	B6	3.50	62.5

Fig 1: *S. mycrophylla* crude exudate gum

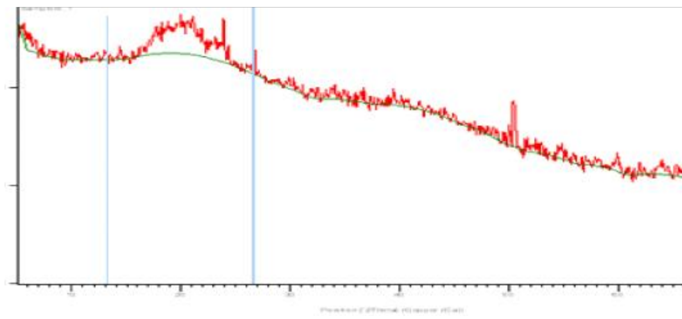

Fig 2: *XRD of S. mycrophylla gum*

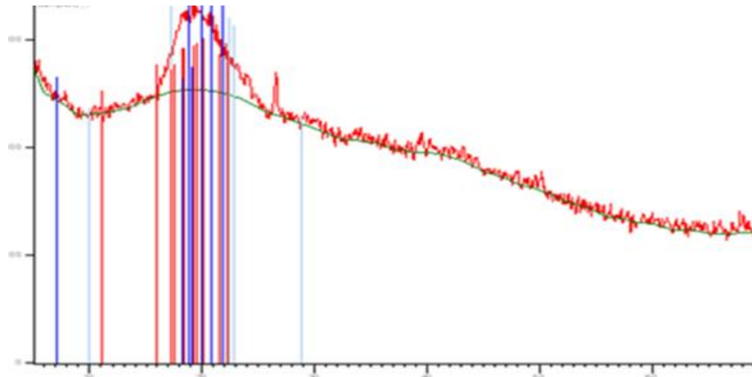

Fig 3: *XRD of Carboxymethyl S. mycrophylla gum*

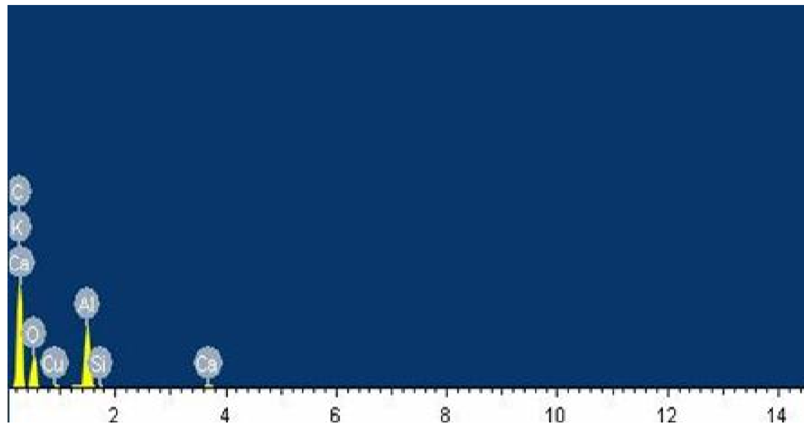

Fig 4: EDX *of Native S mycrophylla*

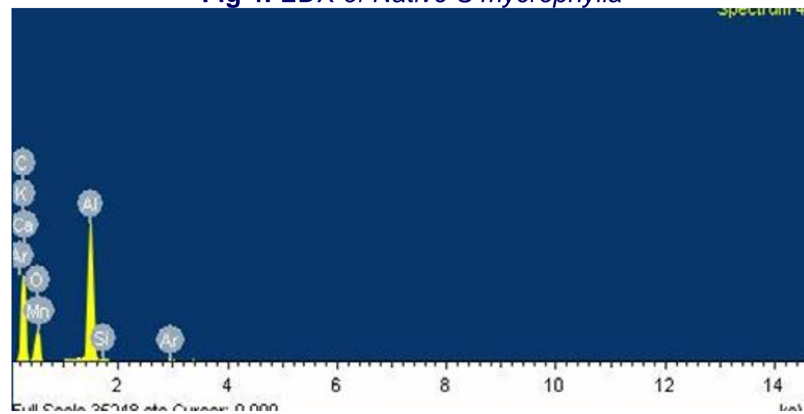

Fig 5: *EDX of Carboxymethyl S. mycrophylla gum*

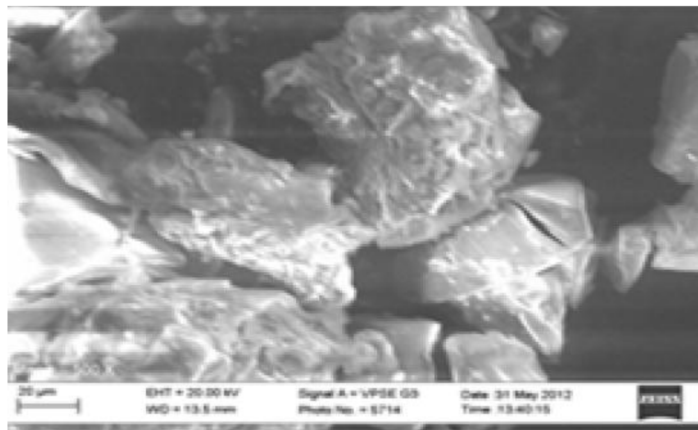

Fig 6: *SEM of Carboxymethyl S. mycrophylla gum*

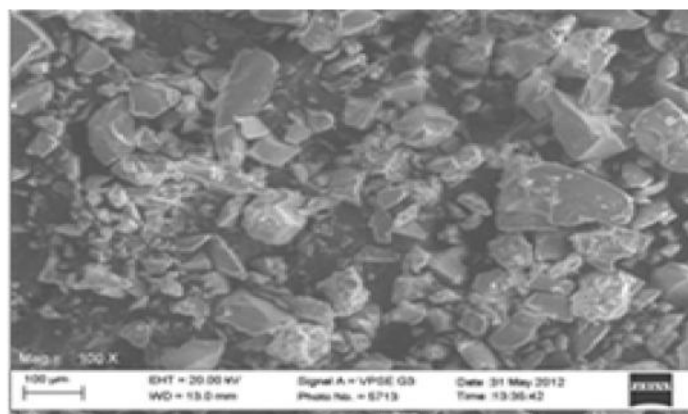

Fig 7: SEM Native *S. mycrophylla gum*

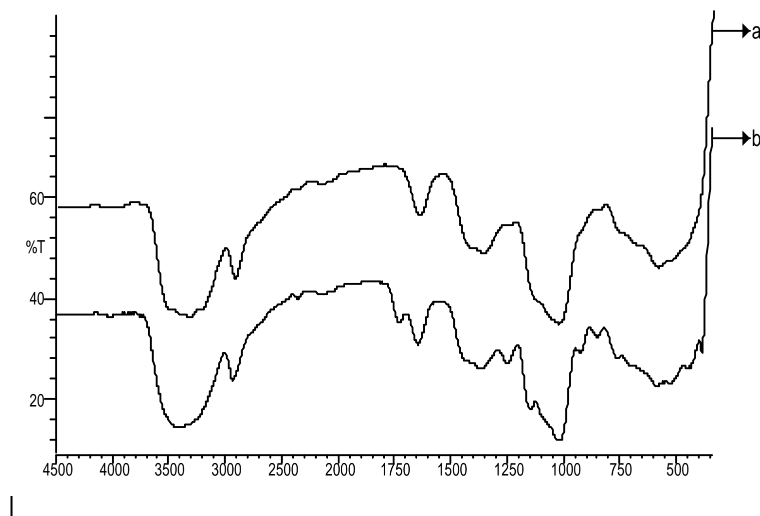

Fig 8: FTIR of (a) unmodified *Sweitenia mycrophylla* gum (b) Carboxymethyl *Sweitenia mycrophylla* gum

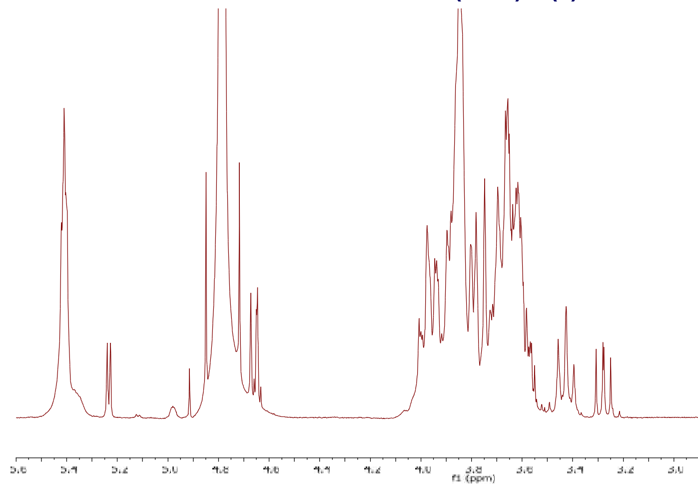

Fig 9: ^{1}H NMR of Native *S. myacrophylla gum*

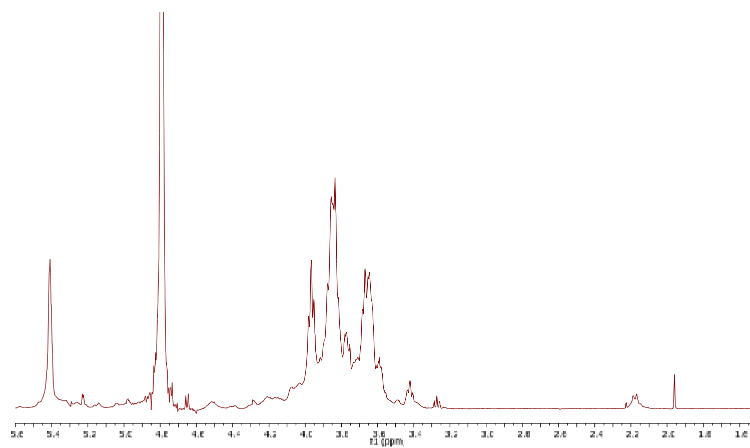

Fig 10: ^{1}H NMR of carboxymethyl *S. mycrophylla gum*

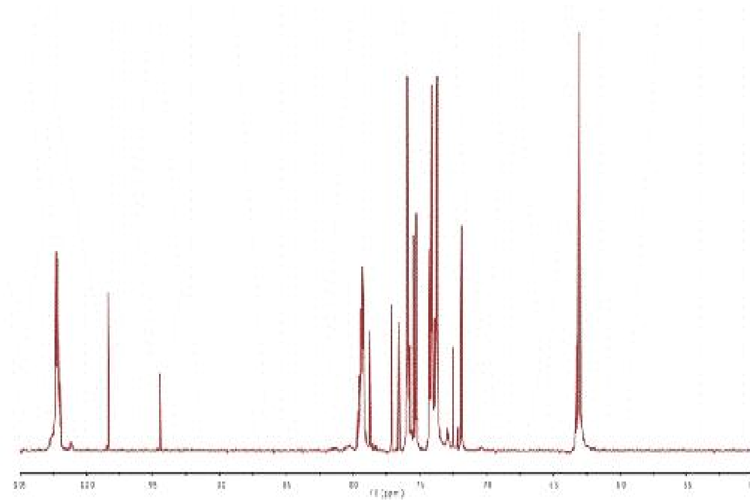

Fig 11: ^{13}C NMR of Native *S. myacrophylla*

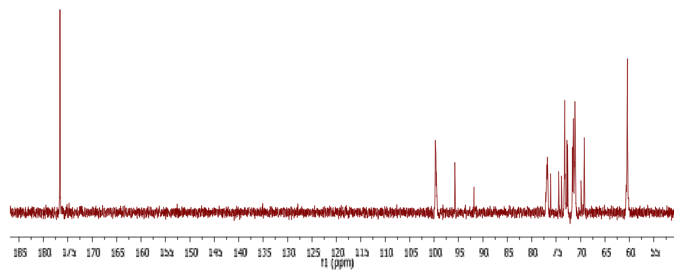

Fig 12: ^{13}C NMR of carboxymethyl *S. myacrophylla*

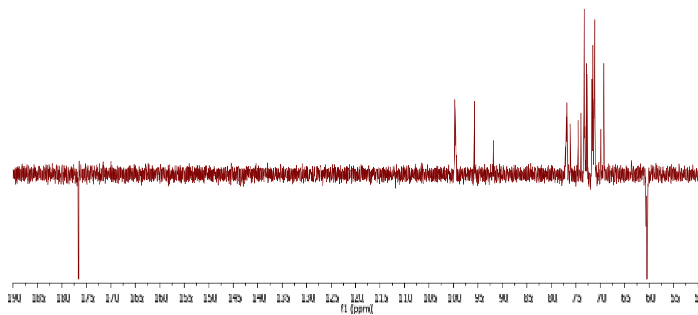

Fig 11: ^{13}C-Dept of carboxymethyl *S. myacrophylla gum*

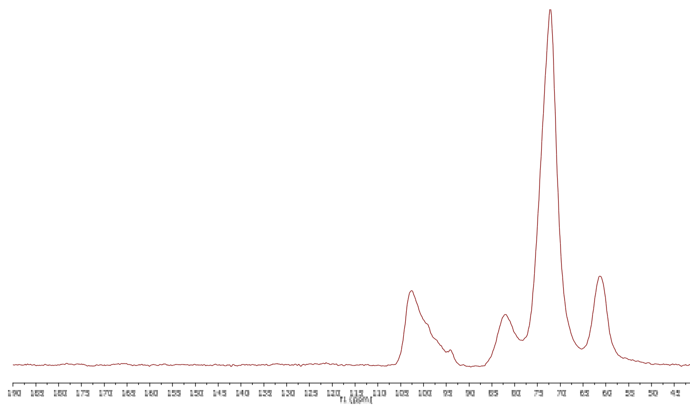

Fig 13: Solid State ^{13}C NMR of Native *S. myacrophylla gum*

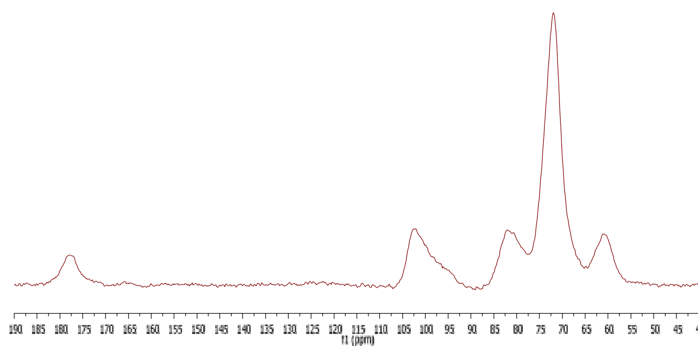

Fig 14: Solid State ^{13}C NMR of carboxymethyl *S.mycrophylla gum*

3.2 Discussion

The physicochemical properties of the native and carboxymethyl S. *mycrophylla* gum is presented in Table 1. The carboxymethyl gum had improved physicochemical properties compared to the native gum, the values of viscosity, solubility and swelling power of the carboxymethyl gum (58.70±0.03 MPaS, 97.94±1.6% at 80^0C and 17.64±0.34%) respectively were higher compared to the values of the native gum (22.50±0.10 MP_aS, 39.50±1.5% at 80^0C and 7.94±0.13%) (Table 1).

Carboxymethylation generally increases the viscosity and water holding capacity of polysaccharide [10]. During carboxymethylation process, the gum granules becomes weak by the introduction of bulkier group like carboxymethyl groups, this allows the penetratin of water into the gum molecules since carboxymethyl groups are hydrophilic in nature [16-19]. [21] reported that introduction of carboxymethyl groups reduces the bond strength between starch molecules (amylase/amylopectin) and thereby increases the swelling power and solubility of the starch granules. This facilitates access of water to amorphous areas, enhancing the viscosity [20].

The superior solubility and swelling power of the carboxymethyl gum compared with the native gum may be due to the presence of hydrophilic substituting groups (OCH_2COO) which allow the retention of water molecules because of their ability to form hydrogen bonds [22-23]. The increase in the viscosity of the carboxymethyl gum may also be due to the steric hindrance exhibited by the alignment of gum molecules [23].

Adding bulky functional groups like carboxyethyl and carboxymethyl groups reduces the tendency of the polysaccharide to recrystallize and make the polysaccharide less prone to damage by heat and bacteria [20]. The SEM analysis of the native gum shows irregular particle size (fig 6) while the SEM of the carboxymethyl gum (fig 7) was found to be fibrilar, indicating loss in particulate morphology that was observed in the native form of the gum. The X-ray diffraction analysis of the native gum (fig 2) shows numerous halves with weak peaks conforming the amorphous nature of the gum while the XRD of the carboxymethyl gum shows more regular pattern with few sharp peaks confirming the level of crystallinity of the carboxymethyl gum (fig 3). The EDX of the native gum sample (fig 4) shows that the gum sample contain various elements such as carbon, potassium, calcium, oxygen, copper, aluminium, silicon, calcium and manganese. The high ratio of carbon, to oxygen indicate the presence of a sugar polymer. Though, virtually all the elements present in the native gum were also present in the carboxymethylated gun (fig 5) but the concentration of these elements increased for the carboxymethyl gum. This may be as a result of the purification of the native gum sample.

FTIR Spectroscopy

The infrared spectra of the native and carboxymethyl gum with DS 0.24 is shown in (fig 8). The broad band between 3600 and 3000cm^{-1} is assigned to O-H stretching and it is due to hydrogen bonding involving the hydroxyl groups in the gum molecule. The bond at around 2922cm^{-1} is assigned to CH_2 symmetrical stretching vibrations around 1600 and 1420cm^{-1}, there is a string absorption peaks for asymmetric and symmetric vibration of COO^- in the spectrum of the carboxymethyl starch. This band confirm the introduction of $–OCH_2COO-$ group into the gum molecule [30].

$^1D^1H$ NMR spectra is presented in chemical shift (ppm) relative to internal reference (Teramethylsilane, TMS). In the proton spectra (fig 5a and 5b), all chemical shifts derived from the polysaccharide are in the range of 1 to 6ppm. The anomeric protons from each monosaccharide gave recognizable signals depending on their and - configurations. However, most of the proton signals fall within a 2ppm chemical shift range (3 to 5ppm) typical of polysaccharides which results in substantial overlap of signals [25-29].

The $^1D^1H$ NMR spectrum (fig 9) of the unmodified gum showed two major peaks at the proton anomeric region which may be attributed to two neutral sugar components of the polysaccharide and thus confirmed that the polysaccharide is composed of a hexasaccharide repeating unit *[30].* The broad singlet and a little peak at 5.4 and 5.2ppm, which are more intense, arise from H-l of sugar residue A (galactose) and is compatible with the expected conformation of –anomer, since –anomer, protons of carbohydrates are in the range of 5 to 6ppm. [25]. The signal for H-l of sugar residue B (mannose) was observed at 4.70 and 4_J92ppm overlaid by D_2O solvent peak at 4.80ppm and corresponds to the monomeric –anomer,While the peaks located at 3.5-4.2 ppm (non-anomeric region) are due to sugar residues H-2 to H-5 [31-32]. Hydrogen bonding decreases the electron density and makes the proton less shielded, this makes the protons to absorb at lower field with crowded signals. **[25-26]. T**he resonance for H-2 to H-6 (fig 9) can be found at 3.2 to 4.2ppm. ^{1}H NMR spectra tend to have overlapping signals in the 3.2 to 4.2ppm region and coupling information is difficult to assign. However, it should be noted that for pyranose rings for proton, ^{1}H signals are generally downfield from the axial ^{1}H, thus for a monosaccharide, an anomeric OH in the -position (which has an equitoria H) has the ^{1}H resonance at 5.3 to 5.8ppm, whereas the -counterpart (having an axial H) resonate at 4.5 to 4.8ppm [33]. The anomeric

proton of residue A (fig 9) had the chemical shift larger than 5.0ppm and very small J-coupling constants of $^3J_{H-1, H-2,}$ suggesting that this residue was -linked , meanwhile the anomeric proton of residue B had the chemical shift smaller than 5.0ppm and relative large J-coupling constant of $^3J_{H-1, H-2}$ suggesting residue B was -linked [34]. The proton assignment of residue A (from H-1 to H-5; 5.42, 3.58, 3.75, 4.00 and 3.95ppm) and residue B (4.71, 4.10, 3.62, 3.80 and 3.75ppm) were obtained [25]. Any substituent on oxygen atom shifts the neighboring protons. This shift usually moves downfield, depending on the substituent in question [27]. The proton chemical shifts are sensitive to the attachment of a non-carbohydrate group such as carboxyl, acetyl, methyl or carboxymethyl groups. Attachment of such groups affect the proton and carbon resonances where the group is located. This place these resonances in a less crowded area of the spectra and helps in the identification of functional groups introduced during modification of polysaccharides. Such appended group may also contain NMR-active nuclei which may give rise to additional splitting due to couplings [36].

In the modified gum $^1D^1H$ NMR spectrum (fig 10) the spectrum for the carboxymethylated gum revealed the occurrence of new peaks at 4.2/4.4 ppm and 2.21/1.89ppm attributed to methylene protons in the carboxymethoxy substituents in position of C-6 of residue A and C-4 of residue B [37-38]. Substitution at oxygen usually moves the ^1H shift downfield. The extent of the shift depends on the nature of the substituent [25].

Although ^{13}C-NMR has a much weaker signal, it has significant advantages over ^1H-NMR spectra in the analysis of polysaccharides, because the chemical shift in ^{13}C-NMR are spread out over a broader range (0-200ppm). This broad distribution of signals helps to overcome the severe overlapping problems associated with the ^1H-NMR spectra [25]. In the ^{13}C spectrum, signals from anomeric carbons appear in the 90 to 105ppm region while the nonanomeric carbons are between 60 and 85ppm for polysaccharide with de-oxygen sugars, the **$-CH_3$** signals appear in a much higher field (15 to 20ppm). The anomeric C-1 carbons are the most diagnostic; thus from C-I alone one can often determine the different types of sequences present and their relative proportions. The resonance of C-2 to C-5 can be found around 65-78ppm. The primary OH (C-6 for pyranoside) resonate at 60-70ppm [25].

Of the two types of sugar residues conformation, signals derived from -anomeric carbons mostly appear in the region of 98 to 100ppm while most of the -anomeric carbons will appear between 101 and 105ppm [39-40]. The signal of carbon atoms having primary hydroxyl groups, such as C-6 appear at a higher field of 60 to 64ppm, while the signals of carbon atoms with secondary hydroxyl groups, the non-anomeric carbons for C-5 shifts by 10ppm to a lower field [25, 39].

The carbon anomeric region of ^{13}C NMR of the unmodified gun (fig 11) showed two major signals at the anomeric region which may be attributed to two neutral sugar components of the polysaccharide which were assigned as C-I of -D-sugar residue A at 98.87ppm and C-I of - D-sugar residue B at 102.1 ppm. The signals due to non-anomeric carbons C-2 to C-5 appear between 60 and 85ppm. The spectrum region of anomeric carbons (102.1 and 98.87ppm) and the methylene carbons (62.50 and 63.50ppm) are well depicted (fig 11). The resonances of the carbon atoms were well resolved (Fig 11) and identified as the resonances of C-2, C-3, C-5 of residue B and C-2. C-3, C-4 and C-5 of residue A (Table 2). These facts are almost identical with gums of other origins [25]. The small peak at around 94ppm is consistence with the chemical shift expected for C-I (OH) in -configuration of residue A ring [39]. The 13C NMR spectrum for modified gum derivatives (fig 12) shows some differences in relation to unmodified gum. The anomeric signals decrease considerably due to chain degradation. A new signal at 174.8ppm was observed for the carbonyl carbon of the carboxymethyl groups [25]. A substitution degree of 0.42 determined by titration indicate a 65.8% of substitution of primary alcoholic groups.

Results of 13C-DEPT NMR 1350 sub-spectra of the unmodified gum and its derivative are shown in (fig 13). The 13C-DEPT NMR experiment was used to identify the methylene groups signals of the carbon atoms bearing two protons which have opposite amplitude to the CH and CH3 carbons.

The 13C-DEPT NMR 1350 spectrum for the unmodified gum showed at a high field two inverted signals (62.45 and 63.65ppm) assigned to methylene carbons (C-6) of the sugar residues. Resonance were assigned with the aid of literature data [25-30]. The spectrum presented only two signal for C-6 of branched-D-mannopyranosyl residue which may indicate according to [27] the presence of residue B triad where the intermediate residue is substituted. The CH2 peaks at 62.45 ppm and 63.65ppm arises from CH2OH of the polysaccharide. This therefore indicate that 6-0 substitution of sugar residue A is present as also found for polysaccharides from other sources [41-43].

In addition to the C-6 resonance observed in 13C-DEPT, CH2 sub-spectra (fig13) as described above, other peaks attributed to residue A units in the region were observed at 98.87, 71.9, 73.0, 74.8, 76.0 and 63.5ppm [42, 44].

In the C-DEPT NMR spectra of the modified gum (fig 13), the signal at 63.45ppm appeared with opposite amplitude to those of CH_3 and CH which can be attributed to the modification of CH_2 primary carbons (C-6). The presence of carboxymethyl groups during carboxymethylation cause an increase in the ^{13}C chemical shift [45].

^{13}C-solid state NMR spectra of the gum and its derivative are shown in (fig 14 and 15). The spectra give line widths which are typical of an armophous natural polymer with broad signal between 64 and 90ppm arising from the bulk of ring of C-OH. This further confirmed the armophous nature of the gum earlier discovered in the x-ray powdered diffraction analysis (XRD) of the gum. The C-4 carbon accounts for high frequent shoulder while C-1 anomeric carbons give the signals between 90 and 110ppm. The shape of this band suggest it is composed of multiple signals but the low resolution suggests the contrary. The peak at 62ppm is assigned to the C-6 of the monosaccharide repeating unit which is attributable to the $–CH_2OH$ belonging to galactose and mannose repeating units [46].

The cluster of resonances around the peak at 72.2ppm and 83.8ppm are assigned to C-2, C-3 and C-5. The peaks at 84.4ppm and 89.0ppm are attributed to C-4 and the absorption peak at 102.1ppm is assigned to C-1 of - mannose in the gum [46].

The modified gum ^{13}C solid state NMR spectrum (fig 15) showed a decrease in signal intensities at both the C-6 and C-4 peaks of the armophous gum sample indicating that the polysaccharide underwent a prefefred degradation of armophous region during modification reactions [47]. The signal at 174.8ppm (fig 5h) is attributed to the carboxymethyl group in the carboxymethylated gum [48-49].

Degree of substitution

The degree of substitution (DS) was determined not based on the total monosaccharide unit but on free unit. The degree of substitution was determined as 0.24. Modified polysaccharides with low DS (<0.1) are used in the food industries since they confer consistency, texture and stability while polysaccharide with high DS (> 0.1) are used in the pharmaceuticals [24]. Close values of DS were obtained for other caboxymethyl polysaccharide in other studies [7, 25, 26].

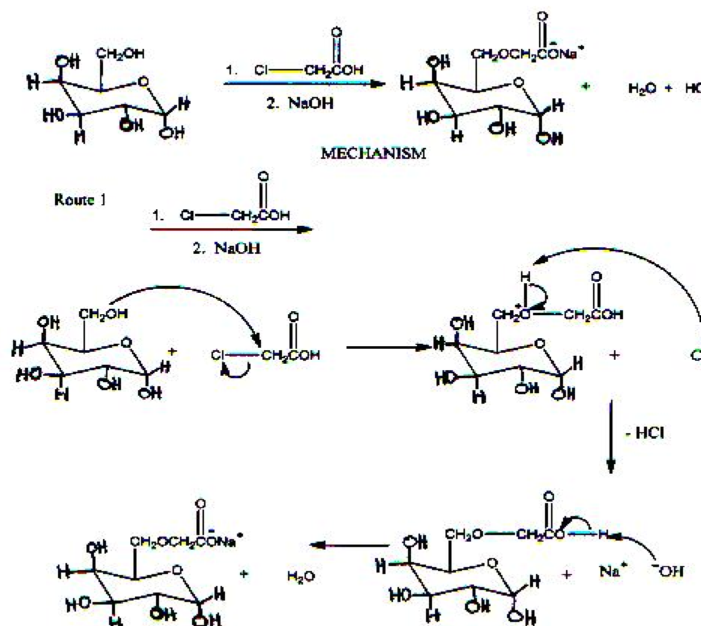

Fig 13: Mechanism for carboxymethylation of *S. myacrophylla*

Conclusion

Carboxymethylated *S.mycrophylla* gum was synthesized and characterized. The new carboxymethyl group was detected by FTIR and NMR analysis. The carboxymethylation occur preferentially at the primary carbons of galactose units as observed by NMR analysis. A higher viscosity, swelling power and solubility was observed for aqueous solutions of carboxymethyl gum in comparism to the unmodified gum. The study confirms that carboxymethylation improves the properties of native gum. It is more attractive because the gum from *P. esculentus* is natural abundant, non-toxic, low cost and regional raw materials. This material may be utilize as binder or disintegrant in solid dosage formulation.

Acknowledgments

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